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Field Study to Obtain Trace Element Mass Balances at a Coal-Fired Utility Boiler

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The report gives results of a study to identify mass flow rates of minor and trace elements from streams of a coal-fired utility boiler (Colbert Steam Plant Unit No. 1). This information was used to obtain a mass balance for 25 elements. The mass balances used inlet and outlet flows associated with three major pieces of equipment: the pulverizer, boiler, and electrostatic precipitator. This provided a mass balance for each element for the various parts of the system. Along with the trace elements which were being measured, organic samples were obtained and analyzed from various streams for polychlorinated biphenyls (PCBs) and polynuclear organic matter (POMs). Thus, the mass balance reflected a fairly complete picture of the boiler under normal operating conditions. The mass balances show that sampling techniques need to be improved. First, the analysis of the vapor-phase samples reported all concentrations below the detection limit for each element. Second, the mass balances of only 10 elements (representing 61% of the total ash flow) closed within + or - 10% for at least two of the three major pieces of the system.

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Trace Elements		Mass Balances	06A	07C
Chemical Analysis	Biphenyl		07D	
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Coal	Organic Compounds		21D	
Combustion	Sampling		21B	14B

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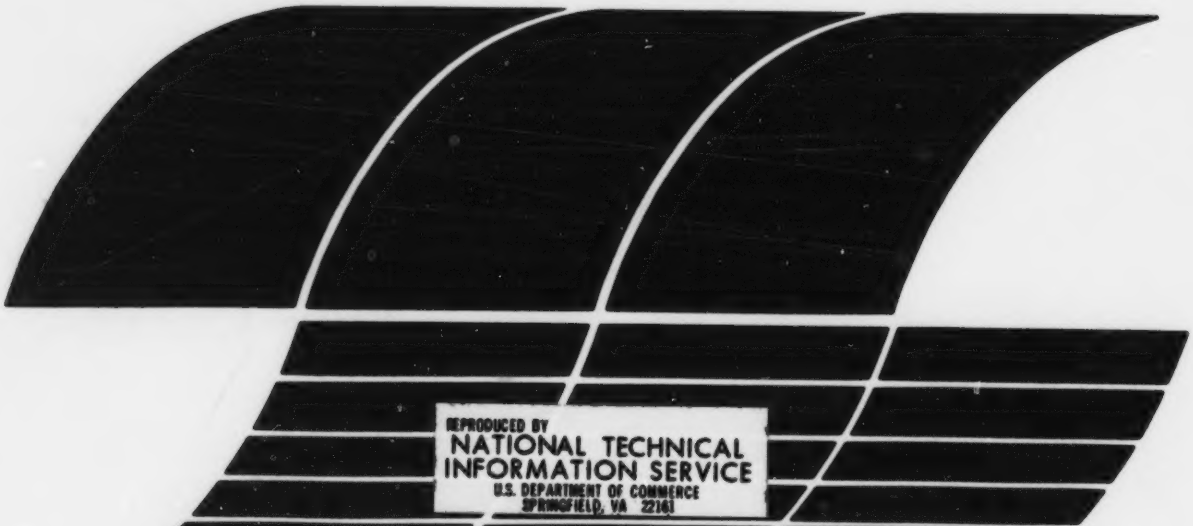

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Field Study to Obtain Trace Element Mass Balances at a Coal-fired Utility Boiler

by

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ABSTRACT

This program was to identify the mass flow rates of the minor and trace elements from the various streams from a coal-fired utility boiler. This information was used to obtain a mass balance for 25 elements. The mass balances used the inlet and outlet flows associated with the three major pieces of equipment; i.e., the pulverizer, boiler, and electrostatic precipitator. This provided a mass balance for each element for the various parts of this system. Along with the trace elements which were being measured, organic samples were obtained and analyzed from various streams for polychlorinated biphenyls (PCB's) and polynuclear organic matter (POM's) by Monsanto Research Corporation and by GCA/Technology Division. Thus, the mass balance presented reflected a fairly complete picture of unit no. 1 (Colbert Steam Plant) under a normal operating condition. The mass balances show that sampling techniques need to be improved. First, the analysis of the vapor phase samples reported all concentrations below the detection limit for each element. Second, the mass balances of only ten elements (represented 61 percent of the total ash flow) closed within ±10 percent for at least two of the three major pieces of this system.

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TABLE OF ABBREVIATIONS

Alk	Alkalinity
A&MF	Ash and Moisture Free
BA	Bottom Ash
ESP	Electrostatic Precipitator
MC	Mechanical Collector
ORP	Oxidation Reduction Potential
PCB	Polychlorinated Biphenols
POM	Polycyclic Organic Material

CONVERSION TABLE

A list of conversion factors for British units used in this report is as follows:

British	Metric
1 micron	10^{-6} meters
1 inch	2.54 centimeters
1 foot	0.3049 meter
1 mile	1.609 kilometers
1 pound	0.454 kilogram
1 ton (short)	0.9072 metric tons
1 gallon	3.785 liters

EXECUTIVE SUMMARY

This study established sampling points around each of the following major pieces of equipment in a fossil-fired steam plant--pulverizer, boiler, and electrostatic precipitator. At these sampling points, the mass flow rate and the concentrations of 25 elements were measured. The measurements included vapor samples from the flue gas duct although vapor phase flows were not used in the mass balance calculations because all concentrations were below detection limits. If only the trace elements are considered, the mass imbalance for the entire system ranged from -6.4 to +12. This range of closure was acceptable for the total trace element material balances. The mass imbalance for each element was quite different. Only ten elements (Table 1) closed within ±10 percent for two or more mass balances around the major pieces of equipment. These ten elements represent approximately 61 percent of the total mass flowrate in the fly and bottom ashes.

Table 1

Elements With Good Material Balances

Si
Al
Mg
Ti
Ba
V
Pb
Cu
Sb
Be

Since the material balance for the total system closed and the analytical methods were adequate for most samples (except vapor samples), it was expected that the balances for each element would close. A problem was encountered with some major elements (i.e., Fe, Ca, K, and Na), and these elements exceeded ±10 percent imbalance in two or more segments of this system; therefore, some doubt is cast on the rest of the trace element material balances.

The size distributions of fly ash were also considered. Cascade impactors were used to evaluate the size distributions of the larger particles, while optical or condensation nuclei counters were used for the submicron particles. Samples from the cascade impactors were combined to allow chemical analysis for three ranges of particle sizes--<1 µm, 1 to 3 µm and >3 µm. Samples were analyzed by TVA and Accu-Lab. These samples allowed verification of elements which tended to concentrate in the smaller particle ranges. The halogens and volatile elements were predominate. The alkali metals (except Ca) also seemed to be concentrated in the smaller particles, while the refractory oxides generally showed no trends relating to particle size. Cr, Cu, and Fe tended to concentrate in the smaller particle sizes of the Brink cascade impactor but showed no trend from the Andersen cascade impactor. (These are listed only as trends because of the large amount of scatter in the data.)

The water side of this project involved measuring the bottom ash and fly ash flow rates from a flume that attached to the inlet of the ash pond. This sampling procedure also required that the inflow sluice water be analyzed as well as the transport water to provide adequate background water quality data for the associated mass flows of each element in the water side of this program. The problem encountered with these measurements was that some of this data indicated a lower bottom ash/fly ash split than the data from the air side. The data from the air side was used in the mass balance when it conflicted with the water side because the air side data was obtained by standard methods. The ESP Hopper measurements from the water side agreed closely with the air side measurement.

Organic sampling for POM's and PCB's was accomplished for various types of samples. GCA/Technology Division collected vapor samples from the inlet and outlet of the ESP and determined the concentration of sulfate in the flue gas from the outlet of the ESP. GCA found the concentration of benzo(a) pyrene to be 0.3 $\mu g/m^3$ and an upper limit to PCB emissions of 1.7 $\mu g/m^3$. Sulfate emissions were 6.47 mg/m^3. The solid and slurry samples (coal, pyrite, and ash) were sent to Monsanto Research Corporation for analysis. No PCB's were detected in any of the samples. POM's were found in all but one sample; however, only two samples contained POM's in appreciable quantities (>1 μg).

This report completes a summary of all sampling that was undertaken at Colbert Steam Plant (unit 1). It was a complete mass balance study intended to help characterize the various waste streams associated with a coal-fired utility boiler. The conclusions that were drawn are supported by our data along with trends that were noted. Some of our conclusions conflict with other reports, especially in the fine particulate analysis. We have only reported what we could support from the data in this report.

SECTION 1

INTRODUCTION

Interest in coal combustion research has increased in recent years due, partly at least, to concern for the environmental effects of coal combustion products. Two tasks of the EPA Interagency Energy/Environment Research and Development Projects, "Characterization of Effluents from Coal-Fired Utility Boilers" and "Fly Ash Characterization and Disposal," comprised this research effort. The "Characterization of Gaseous Emission" task was concerned with atmospheric emission of trace constituents in coal. The "Fly Ash Characterization" task consisted of investigating the chemical constituents of liquid and solid effluents from the unit. Because the combustion of fossil fuels is known to generate a multitude of chemical species that may be discharged into the environment as combustion products, and because the use of coal is expected to increase during the next two or three decades, attention was given to obtaining information on the contribution of power plants to the environmental loading of these chemical substances. This study may in turn lead to a more complete understanding for the distribution of these species and ultimately to the development of better means to control their discharge to the environment.

Studies (1-6) have been reported which undertook to determine the trace element composition in coal and in fly ash collected at various locations along the flue gas stream and to delineate the mass balance of trace elements about the power plant systems. These studies have succeeded in demonstrating some aspects for the flow of trace elements in the flue gas and the distribution of these elements in various fractions contained in the fly ash particles. However, the fates of many of the trace elements in the vapor phase were not well known primarily due to inadequate sample collection techniques. Additionally, there were no previous studies focused on the water side. This study utilized the water side data to provide a more complete understanding for the fate of trace elements in effluents (whether liquid, solid, or gaseous).

In view of the concern with toxic trace elements that may be released from fossil-fuel combustion, TVA conducted a research program to quantify and characterize such combustion products from all effluent streams from one of its coal-fired power plants--specifically, Colbert Steam Plant in northwestern Alabama.

SECTION 2

CONCLUSIONS

The following conclusions are based on the results from an 8-day field study conducted on a TVA steam plant (Colbert). The test boiler was a wall-fired utility boiler rated at 200 MW, and the coal was mined from western Kentucky.

1. The mass balance around the pulverizer accounts for approximately 94 percent of the substance in coal. After making appropriate allowances for oxygen and silica content, the sum of the 27 trace elements considered in this study closely approximates the ash content of coal.

2. The high variability in the data at the electrostatic precipitator (ESP) outlet, compared to other sampling points, suggests that difficulty in analyzing small sample sizes was primarily responsible for spurious results or that the sample was not representative.

3. Fly ash has a much more pronounced effect on raw sluice water quality than does bottom ash. Ca, B, Se, Cr, Al, F, and $SO_4^{=}$ concentrations and pH, alkalinity, and conductivity experienced relatively large increases, especially in the fly ash sluice water. Zn and Cu appear to have been partially removed from the dissolved portion of the sluice water during bottom ash sluicing; and Cu, Mg, and Si appear to have been reduced from the solution during fly ash sluicing.

4. Since there were no essential differences in the levels of Ca, Mg, $SO_4^{=}$, Si, and Hg for the 45-minute and 14-hour supernatant samples of fly ash or bottom ash sluice water, it is suggested that most chemical reactions between ash and water occurred within 45 minutes from the start of the sluicing.

5. Based on the particulate sizing and optical particle counting results, it may be concluded that the ESP removed a large percentage of particles greater than 3.5 µm in diameter. One half the total mass of particles leaving the system in stack gases were smaller than 3.5 µm. Because particles with a diameter of 0.4 µm comprise 80 percent of the total particle count at both the ESP inlet and outlet. It is suggested that the elemental mass composition of particles <3.5 µm should be studied further.

6. Our results of the fine particulate chemical analysis indicate that elements generally considered volatile tended to concentrate in fine particulate smaller than 3 µm. The alkaline earth and alkali metal elements also tended to concentrate in the fine particulate smaller than 3 µm. Most of the remaining elements showed no discernable trends or preference for particle size.

7. No polychlorinated biphenyls were detected in any of the ash sluice samples; only two out of eight samples contained polycyclic organic matter in appreciable quantities (>1 μg).

8. The aggregate material balance for the trace element flows over the entire 8-day sampling period had the smallest error around the pulverizer (+3.7 percent error), a +5.8 percent error around the ESP, and the largest error around the boiler (-6.8 percent). On an aggregate basis this would indicate adequate sampling and analytical procedures, but detailed examination of individual trace elements indicated this error was sufficiently large to mask their behavior.

9. Especially noticeable between the whole coal and pulverized coal flow rates, the system flow rates were extremely different and inconsistent throughout the system on days 1 and 8. This difference may be due to a flow rate estimation problem and/or a detection limit problem.

10. Fifteen of the twenty-five elements had mass imbalances in excess of ±10 percent for two of the three loops in the system. Surprisingly, iron, calcium, potassium, and sodium fell into this category. Because these four elements are relatively abundant in coal, these results were unexpected. Removal of tests 1 and 8 did not improve the results. Ten elements (approximately 61 percent of the total trace element flow) had a material balance within ±10 percent for at least two of the three loops in the system.

11. Of the pulverizer, boiler, and ESP loops, the largest variability was associated with the ESP and appeared to be both a problem of day-to-day variability and the difficulty of collecting a sample and analyzing the vapor phase and fine particulate data. Large variability was consistently seen in the ESP outlet data, the pyrite data, and the bottom ash data.

12. Two groups of elements, which were distinctly identifiable through the system, followed similar trends in their distribution in the waste streams. The first group consisted of lead, iron, manganese, potassium, silicon, and cobalt. The second group consisted of beryllium, vanadium, chromium, magnesium, copper, titanium, and zinc. Not all expected groupings could be identified due to the coarseness of the data.

13. The vapor phase sampling and analytical procedures were inadequate. Lower limits of detectability in the vapor phase consistently exceeded the total flow rate of the element in the whole coal. Chlorine, fluorine, and selenium were three elements whose mass balances around the boiler and ESP could be drastically improved through better vapor phase data and more flow rate sampling around the boiler and ESP.

14. Contamination from stainless steel particles may have occurred during the entire sampling period as chromium, nickel, and manganese exhibited large gains through the system.

SECTION 3

RECOMMENDATIONS

1. Since the product formed by ashing coal in the laboratory could be qualitatively and quantitatively different from that formed in a boiler, false estimates of total ash flow rates may result. Therefore, it is recommended that work be done to determine if ash produced in the laboratory is substantially different from ash produced in a boiler.

2. Sampling procedures need to be improved for these elements--F, Cl, Sb, As, Be, B, Hg, Se, S, and Pb. Large amounts of these elements are unaccounted for in the mass balance.

3. It is strongly recommended that sulfur be included with Fe and Al as a monitored element in all flows. The instrumentation, chemical behavior, and combustion behavior of sulfur would serve as an important check on sampling procedures, system behavior, flow rates, and accuracy.

4. Variability of power plant operating conditions is a factor that must be recognized. In order to identify the behavior of trace elements under these various conditions, a longer sampling program is recommended.

5. The addition of measured flow rates around the boiler and ESP could drastically improve the mass balance estimates and, hence, the understanding of the behavior of trace elements through the system.

SECTION 4

EXPERIMENT

This study began in August 1976, at the Tennessee Valley Authority's Colbert Steam Plant located in northwest Alabama on the Tennessee River. Because of manpower limitations, a contractor experienced in stack sampling, Midwest Research Institute (MRI), was selected to conduct the sampling program for trace elements in the boiler flue gases. The GCA Corporation, under contract to the Environmental Protection Agency (EPA), sampled the adjacent electrostatic precipitator (ESP) outlet duct "A" on the same unit for polycyclic organic matter. TVA personnel conducted all other sampling efforts during this study.

All tests were conducted with the unit at steady operating conditions near full load (approximately 180 MW) throughout each daily test period. The unit was brought to test conditions and allowed to stabilize for a minimum of one hour before testing began. Boiler soot blowing was done each morning at least one hour before testing began, and air preheater soot blowing was done on the midnight shift. Flue gas temperature was near the design temperature of 340°F for the flue gas entering the ESP.

BOILER DESCRIPTION AND OPERATION

The Colbert unit 1 (Figure 1), which was selected for this study, is a split-wall, pulverized coal-fed, wall-fired, dry-bottom boiler manufactured by Babcock and Wilcox Company. Eighteen burners are arranged in three horizontal rows of 6 burners each. The unit has a rated capacity of 1,280,000 pounds of steam per hour and a rated 200-MW capacity at a coal fuel input of approximately 76 tons per hour. The steam generator is served with a Ljungstrum regenerative single-pass air preheater and by a Lodge-Cottrell double-chamber electrostatic precipitator with three fields, each nine feet deep. The nameplate design data for the precipitator specifies a collection efficiency of 97 percent with a gas flow of 906,000 ft^3/min at 340°F flue gas temperature.

Coal is fed continuously from the coal bunker, across a coal-scale system, to the pulverizer, where it is ground to a consistency resembling that of talcum powder. As the coal is pulverized, hard pyritic material is rejected automatically by the mill and is collected in hoppers adjacent to the pulverizers. The pulverized coal is then transported to the furnace burners by the hot primary combustion air, where it is burned instantaneously at temperatures in the range of 2700°F-3200°F.

The solid byproducts from coal combustion can be generally classified as bottom ash, fly ash, and slag. The bottom ash and slag [collectively referred to as bottom ash (BA)] fall to the bottom of the furnace, where they are collected and removed by high-pressure water jets. The fly ash is carried on through the boiler in the hot gas stream and passes through the air preheater where the gases are cooled to approximately 400°F. The gas stream, with the entrained fly ash, continues on through

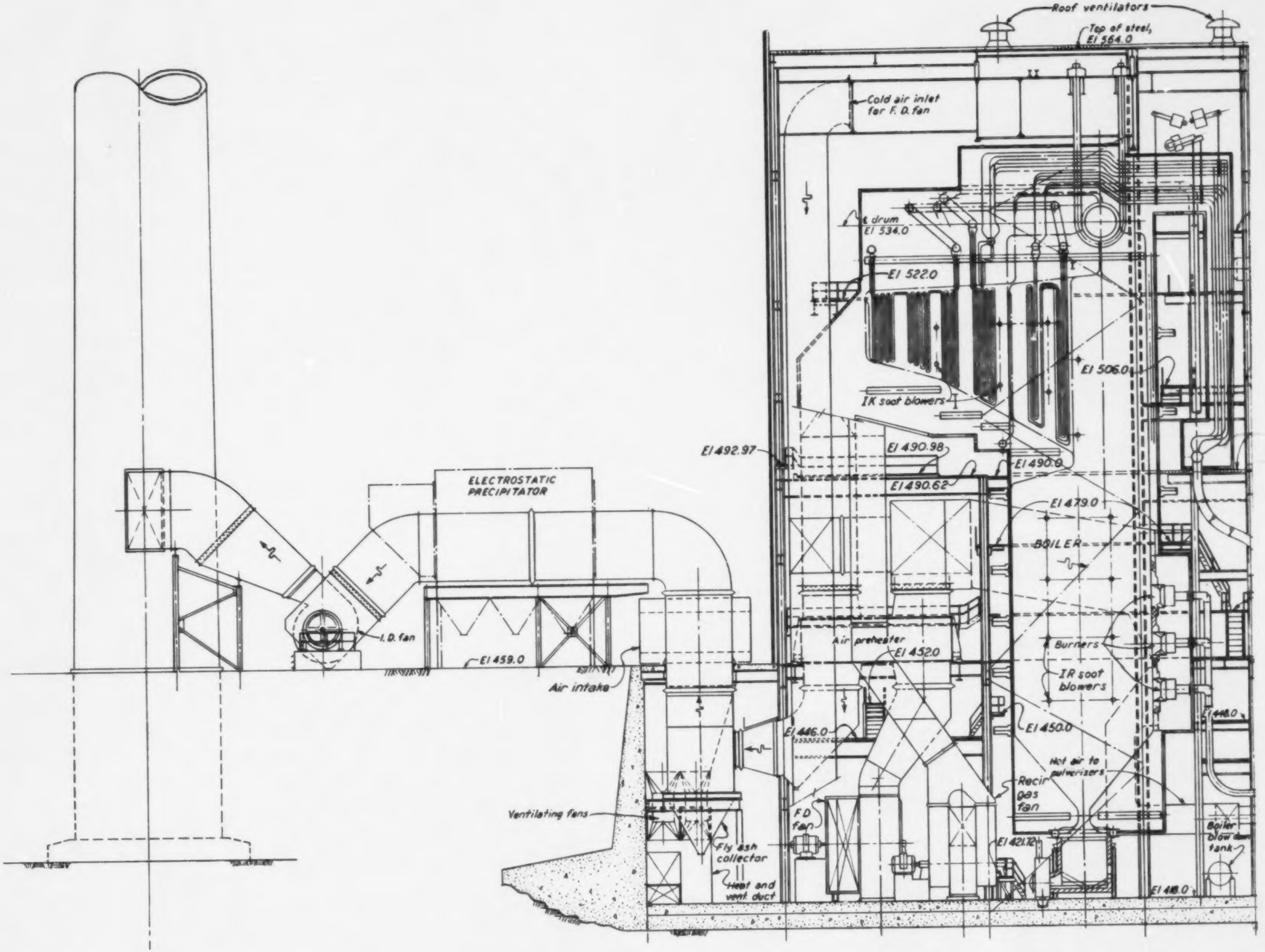
Roof ventilators
Top of steel, El 564.0
Cold air inlet for F. D. fan
℄ drum El 534.0
El 522.0
El 506.0
IK soot blowers
El 492.97
El 490.98
El 490.0
El 490.62
El 479.0
BOILER
ELECTROSTATIC PRECIPITATOR
I. D. fan
El 459.0
Air intake
Air preheater
El 452.0
Burners
IR soot blowers
El 450.0
El 446.0
Hot air to pulverizers
Recir gas fan
FD fan
Ventilating fans
Fly ash collector
Heat and vent duct
El 421.72
El 418.0
El 448.0
Boiler blow down tank

Figure 1. Colbert unit 1.

mechanical fly ash collectors (MC) that have had the collection vanes removed, where a small percentage of fly ash is removed by gravitational settling. Upon exit from the mechanical collectors, the gas stream enters the ESP which removes most of the remaining fly ash (97 percent) and collects it in hoppers. The gases and any remaining fly ash exit the system through the stack.

Bottom ash, pyritic material, and the small amount of fly ash collected in the mechanical collectors are sluiced to a common sump. This slurry then passes through clinker grinders and is pumped to the ash settling pond. Fly ash collected in the ESP hoppers is removed by a water-operated exhauster and sluiced to the ash settling pond as a slurry.

SAMPLING PROCEDURES

Basically two different sampling efforts were carried out simultaneously during this test. One effort focused on the gaseous and particulate emissions from the boiler. The second effort was directed at characterizing the various ashes that were removed from the process at various points in the system. Figure 2 is a block diagram of the process with the various sampling points identified. Table 2 is a summary of the samples taken and the chemical constituents or parameters for which they were analyzed. Table 3 is a listing of the trace elements investigated. The two efforts overlapped at the ESP, where two samples of the hopper ash were taken.

Because of financial constraints, the gaseous emissions study was conducted on only one-half the unit--the "B" side; and hopper ash samples were, therefore, taken on only that half of the ESP. The ash characterization effort took a sample across the entire unit. The following material is a description of the sampling procedures used at each sampling point identified in Figure 2.

Coal

Whole Coal--

Coal flowing from the coal bunker to the test boiler passes across one of six coal scales serving the boiler. These scales are designed for a 500-pound-per-dump capacity and are equipped with counters for recording the number of dumps. The scales also have a bypass arrangement for feeding coal directly to the pulverizers in the event of a scale malfunction. Coal flow rates for the test periods were based on these scale counters, and estimates were made for those periods when the bypass arrangement was in use.

The whole coal samples were taken from each of the six coal scales serving the test boiler. A sampling ladle was used to collect a grab sample at 15-minute intervals from each of the six coal scales. All the grab samples for a given test were composited in a large plastic container and, at the end of each test, the total sample was ground to No. 4 mesh and then riffled into a quart-size proportional homogeneous sample. This sample was put into a labeled glass jar.

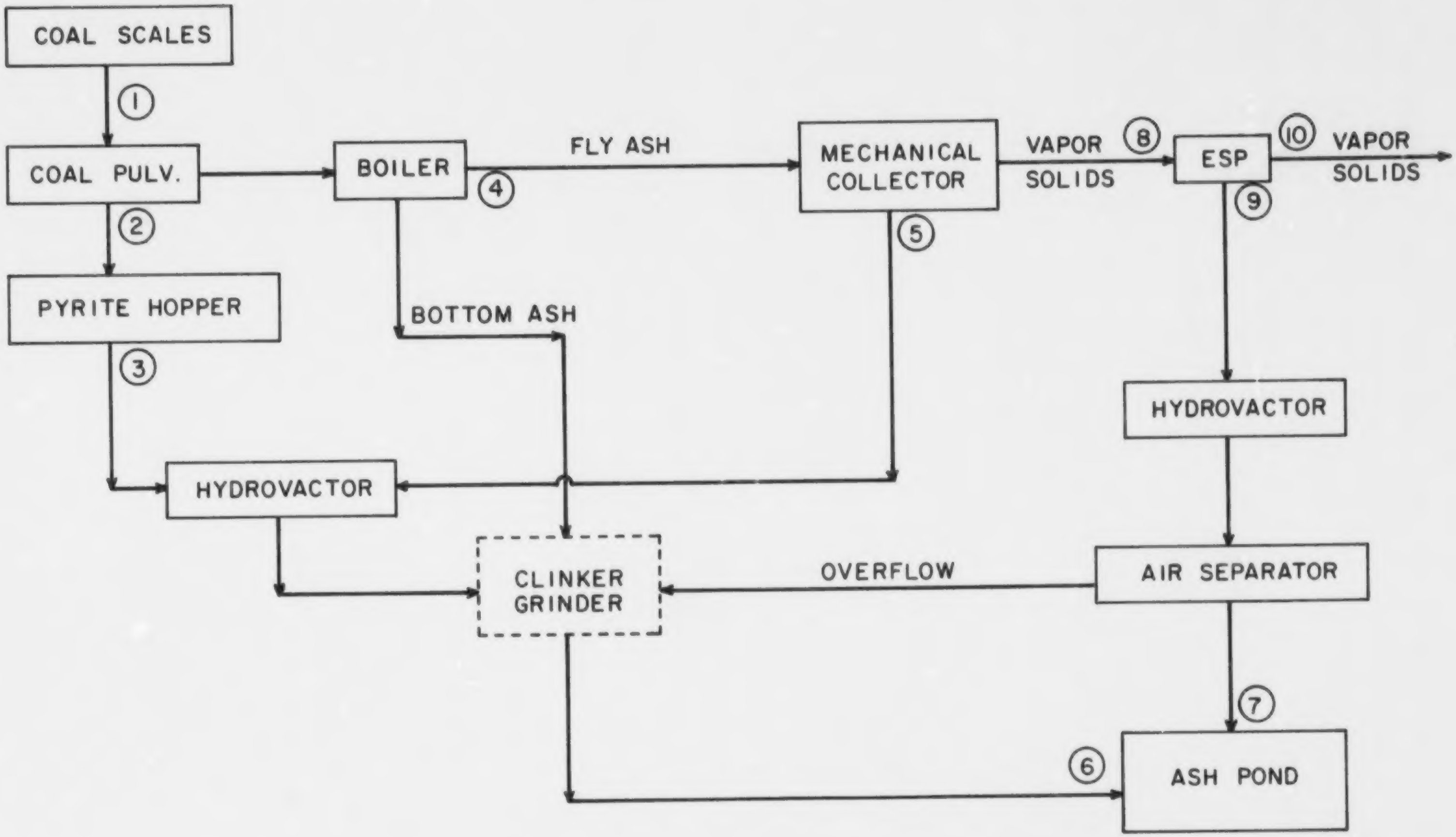
COAL SCALES
①
COAL PULV.
②
PYRITE HOPPER
③
BOILER
④
FLY ASH
BOTTOM ASH
MECHANICAL COLLECTOR
⑤
VAPOR SOLIDS
⑧
ESP
⑨
⑩
VAPOR SOLIDS
HYDROVACTOR
HYDROVACTOR
CLINKER GRINDER
OVERFLOW
AIR SEPARATOR
⑦
⑥
ASH POND

Figure 2. Coal and ash flow diagram.

TABLE 2. SUMMARY OF SAMPLES AND CONSTITUENTS DETERMINED

Sample - Location	Constituents Analyzed
Coal - 1, 2	Trace elements,* proximate and ultimate analysis
Pyrites - 3	Trace elements
Bottom Ash, Dry Ash - 6	Trace elements, major oxides (Al, Ca, Fe, K, Mg, Na, S, Si, and Ti)
,45 Minute Supernatant - 6	Ca, Mg, Hg, SO_4, Si, pH, AlK, ORP, Conductivity
,14 Hour Supernatant - 6	Trace elements, SO_4, pH, AlK, ORP, Conductivity
Boiler Outler - 4	CO, CO_2, O_2
Mechanical Collector Ash - 5	Trace elements, major oxides
ESP Ash, Dry Hopper Ash - 9	Trace elements
,45 Minute Supernatant - 7	Ca, Mg, Hg, SO_4, Si, pH, AlK, ORP, Conductivity
,14 Hour Supernatant - 7	Trace elements, SO_4, pH, AlK, ORP, Conductivity
ESP Inlet Duct, Total Particulate - 8	Trace elements (except Na, B, S, Si)
,Vapor Phase - 8	Trace elements (except Na, B, S, Si)
,Particulate Sizing - 8	Trace elements (except Na, B, S, Si)
ESP Outlet Duct, Total Particulate - 10	Trace elements (except Na, B, S, Si)
,Vapor Phase - 10	Trace elements (except K, Na, B, S, Si)
,Particulate Sizing - 10	Trace elements (except B and S)
Raw Sluice Water, Total	Trace elements, SO_4, SS, pH, AlK, ORP, Conductivity
,Dissolved	Trace elements, SO_4, TDS

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*Trace elements are those listed in Table 3.

TABLE 3. MAJOR AND TRACE ELEMENTS IN UNDER CONSIDERATION IN THIS STUDY

Aluminum (Al)
Antimony (Sb)
Arsenic (As)
Barium (Ba)
Beryllium (Be)
Boron (B)
Cadmium (Cd)
Calcium (Ca)
Chlorine (Cl)
Chromium (Cr)
Cobalt (Co)
Copper (Cu)
Fluorine (F)
Iron (Fe)
Lead (Pb)
Magnesium (Mg)
Manganese (Mn)
Mercury (Hg)
Nickel (Ni)
Potassium (K)
Selenium (Se)
Silicon (Si)
Sodium (Na)
Sulfur (S)
Titanium (Ti)
Vanadium (V)
Zinc (Zn)

Pulverized Coal--

Pulverized coal samples were taken hourly using a cyclone sampler to traverse one of three coal transport ducts from each of the six pulverizers. All the samples for a given daily test were composited and, at the end of the day, each composite sample was mixed, reduced to a quart-size sample, and sealed in a dry glass jar.

Pyrites

At the start and end of a test, the pyrite hoppers were emptied. Figure 3 shows the sluicing schedule that was used during this test for pyrites, mechanical collector, bottom ash, and the ESP. At the end of the test, a grab sample was collected from each of the six pyrite hoppers and a measurement of the depth of the pyrites in each of the hoppers was made. These measurements were used to calculate the total volume of pyrites collected during the daily test period. At the end of each day, the pyrite grab samples for a given test were composited, ground to No. 4 mesh, reduced to a quart-size daily sample, and sealed in a glass jar.

Bottom Ash

Bottom ash was removed from the boiler, sluiced to the ash pond prior to each test, and then allowed to accumulate in the boiler during the test. At the end of the test, the bottom ash was again sluiced to the ash pond unless operational constraints required bottom ash sluicing prior to the end of the test. Collection of a daily representative grab sample from the bottom of the furnace was infeasible; therefore, all bottom ash samples were taken as the ash was being sluiced to the ash pond (Figure 2). A sampling flume (Figure 4), designed to provide a homogeneous sidestream from which representative samples could be taken, was installed on the end of the transport pipe. The sidestream flow of approximately 360 gallons per minute represented one-tenth of the total sluice flow. Bottom ash slurry samples were taken at 30-second intervals during sluicing, composited in 30-gallon plastic containers, and allowed to stand undisturbed.

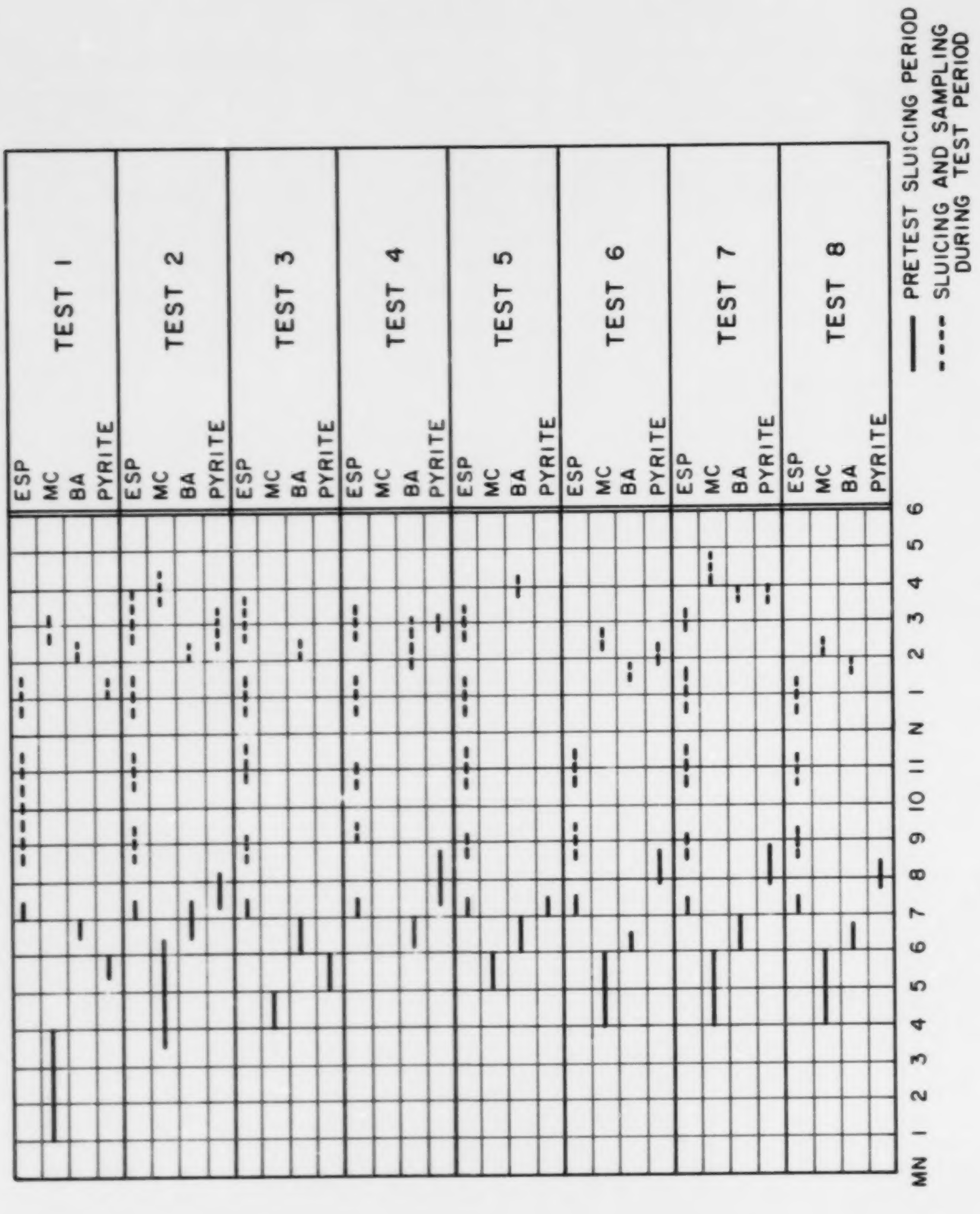

Figure 3. Ash sluicing test schedule.

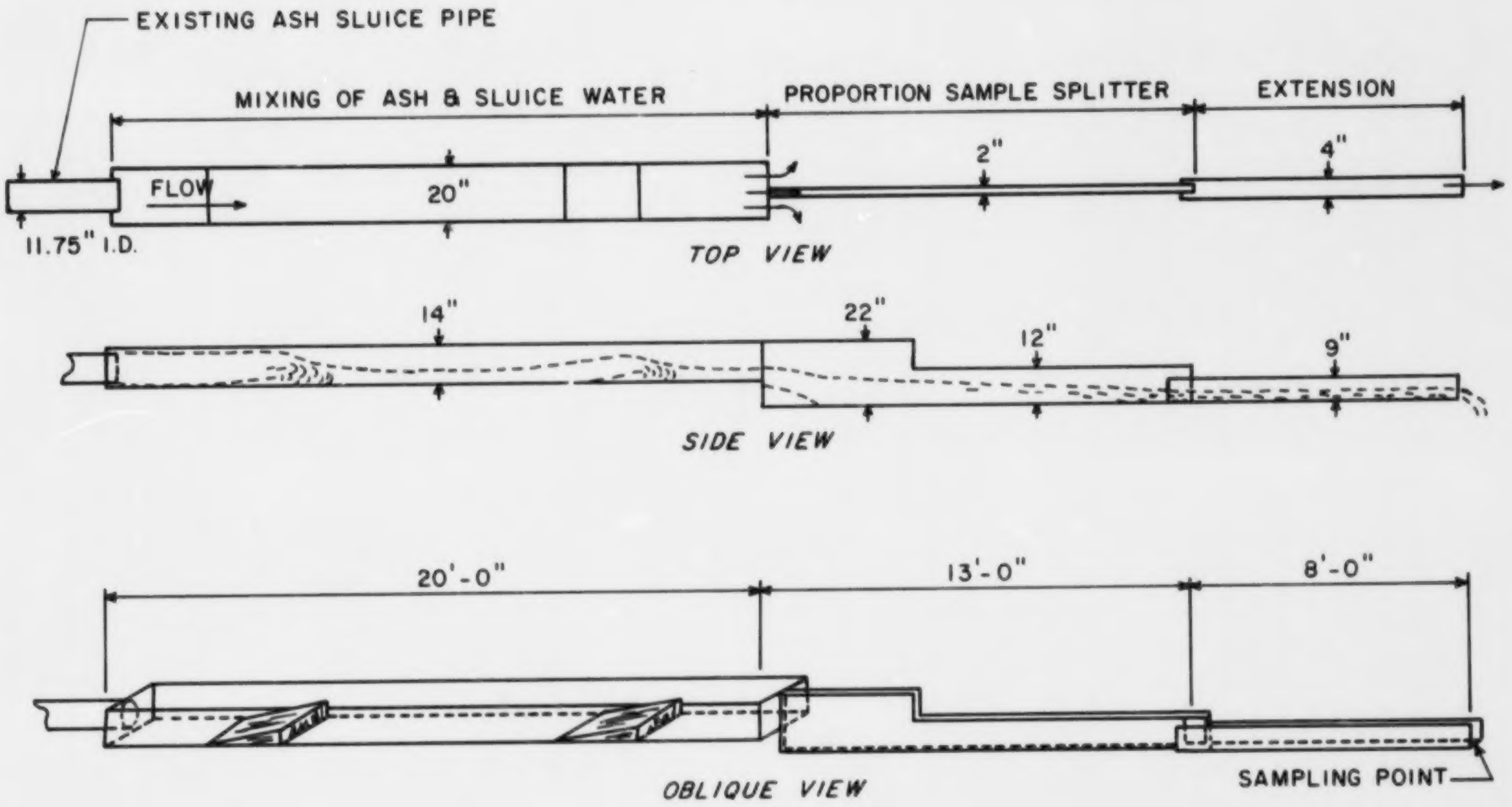
EXISTING ASH SLUICE PIPE
MIXING OF ASH & SLUICE WATER
PROPORTION SAMPLE SPLITTER
EXTENSION
FLOW
20"
2"
4"
11.75" I.D.
TOP VIEW
14"
22"
12"
9"
SIDE VIEW
20'-0"
13'-0"
8'-0"
SAMPLING POINT
OBLIQUE VIEW

Figure 4. Bottom ash sampling flume.

After a 45-minute settling period, a water sample was siphoned from the surface of the composite sample and analyzed in the field for pH, alkalinity, Oxidation Reduction Potential (ORP), and conductivity. A portion of this supernatant was filtered through a 0.45-μm millipore filter and preserved for laboratory analysis. After the large composite sample had remained quiescent for 14 hours, all the water was siphoned from the settled solids and the decanted water volume was measured. Samples of this 14-hour supernatant underwent the same field handling and field analysis as the previous 45-minute supernatant sample. Table 4 gives the liquid sample preservation procedures that were used in the field when taking all of the liquid samples. All of the settled solids were placed in a plastic container and sent to the laboratory for analysis. Composite samples of the first four days and of the last four days were also taken.

Boiler Outlet Duct

The major gaseous components of the flue gas were measured at the boiler outlet with instruments installed on a mobile TVA van. The instruments installed included: a DuPont Model 400 nondispersive UV spectrophotometer for SO_2, a Thermo Electron model 10A chemiluminescent monitor for NO and NO_x, a Beckman Model 864 IR analyzer for CO and another for CO_2, a Beckman Model 742 polarographic sensor for O_2, and a Beckman Model 400 flame ionization analyzer for hydrocarbon. The hydrocarbon analyzer was not used in this study because of technical difficulties. The CO_2 analyzer malfunctioned, and no data on this constituent were obtained. However, ORSAT measurements of CO, CO_2, and O_2 were made at the ESP inlet duct; these measurements compared favorably with the van instrumentation measurements of CO and O_2.

Five sampling probes to a common sample header were used to traverse the duct at the entrance to the air heater through five ports at three traverse points (depth) to draw representative samples. The samples were conveyed through Teflon tubing to the instruments located in the van for measurements of SO_2, NO-NO_x, CO, and O_2. Gas monitoring at the boiler outlet was done simultaneously with the sampling efforts at the ESP inlet and outlet ducts.

Mechanical Collector Fly Ash

The mechanical collector hoppers were emptied at the start of each test and at the end of a test run. Dry fly ash samples were taken from a sampling port located in the bottom of each of the eight mechanical collector hoppers. A tubular thief sampler was used to collect the samples at 30-second intervals as each of the eight hoppers were emptied. Samples were composited for each hopper in plastic bags. The ash samples representing each hopper were composited into a daily sample, based on the percentage of the total mechanical ash collected in a given hopper, by taking weighed portions from each bag. The percentage of total ash in a hopper was estimated by the percentage of the total sluicing time required to empty a given hopper. These composite samples were sealed in a glass jar.

TABLE 4. PROCEDURE FOR PRESERVATION OF WATER SAMPLES

Constituent	Sample Container	Sample Preparation and Preservative
A. Total species		
Al, Sb, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni,	500-ml glass bottle (HCl clean)	Sample was put in container that had been predosed with 2-ml of 1+1 HNO_3.
B, Cl, F, Na, SO_4, SS	1-quart plastic cubitainer (new)	Stored at 4°C.
B. Dissolved species		
Al, Sb, As, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mg, Mn, Hg, Ni, K, Se, Ti, V, Zn	500-ml glass bottle (HCl clean)	Sample was filtered through 0.45 μm millipore filter pad and then put in the sample container that had been predosed with 2-ml of 1+1 HNO_3.
B, Cl, F, Na, SO_4, SiO_2, TDS	125-ml plastic bottle (HCl clean)	Sample was filtered through 0.45 μm millipore filter pad and then put in the sample container.

Also, composite samples of the first four days and of the last four days were taken.

Electrostatic Precipitator Hopper Ash

Prior to each test the ESP hoppers were emptied. The large volume of fly ash collected during the test necessitated emptying the hoppers at 2-hour intervals during the daily test period. Dry fly ash samples were collected from sampling ports located in the bottom of each of the 12 hoppers. A tubular thief sampler was used to collect the samples at a rate of one per minute for each hopper as they were emptied. These samples were composited in a manner identical to the mechanical collector samples so that there were four composite samples (one for each sampling period) at the end of an 8-hour day. As mentioned previously, two composite samples were taken at the hoppers--one over the entire ESP, and the other over only the "B" side of the ESP.

In addition to the dry ESP fly ash samples, a slurry sample was collected at the ash pond. Two 100 ml samples were taken at 15-second intervals as the fly ash slurry flowed from the end of the sluice pipe. The samples were composited during each sluicing period in 30-gallon plastic containers and allowed to settle. After 45 minutes of settling, a water sample was siphoned from the top of the container and analyzed in the field for pH, alkalinity, ORP, and conductivity. Also, a portion of the sample was filtered through a 0.45-µm millipore filter and preserved for laboratory analysis. After 14 hours of settling, the supernatant was siphoned from the settled solids and the total volume was measured. Samples of this 14-hour supernatant underwent the same field analysis and handling as the 45-minute supernatant did. The settled solids were placed in a plastic bag and stored for future analysis.

Electrostatic Precipitator Inlet and Outlet Ducts

A number of different sampling techniques were utilized in sampling the ESP inlet and outlet ducts. A description of the equipment used can be found in Appendix A.

Raw Sluice Water

Raw sluice water samples were collected for each daily test by setting a valve, located in the sluice water supply line, to drip at a rate sufficient to fill a 5-gallon cubitainer during each daily test period. A sample of the inflow water was analyzed in the field for pH, alkalinity, ORP, and conductivity. Two additional samples, one for suspended solids and the other for dissolved solids, were taken and sealed in sample jars. The dissolved solids sample was filtered through a 0.45-µm millipore filter before being sealed in the sample jar.

METHODS OF CHEMICAL ANALYSIS

A number of different chemical analyses were performed on the various samples taken during this test. The techniques used for the quantitative determinations were based on:

1. Atomic Emission Spectroscopy
2. Atomic Absorption
3. Gravimetry
4. Potentiometric Titration
5. Ion Chromatography
6. Specific Ion Electrode
7. Differential Pulse Anodic Stripping Voltametry
8. Colorimetry
9. Titrimetric Analysis
10. Turbidmetric Analysis

The procedures used are described in detail in Appendix B.

As a check on the chemical analysis procedures, certified NSB Standards 1632 coal and 1633 fly ash were analyzed in parallel with the test samples. (These data are presented in Appendix B.) Appropriate blanks were run on the various collection substrates to correct for trace elements contained in the substrates. An aliquot of each liquid reagent used in each sampling train was analyzed for trace elements. In each case the value obtained for an element in the blank was subtracted from the corresponding element in the test sample. If the sample value was not at least twice the value of the blank, the difference was reported as a "less than" number for that element. Semiquantitative analysis, based on spark source mass spectrometry for trace elements in some of the fine particulate impactor samples, was performed by Accu-Labs, Inc., so that a comparison of methods and results could be made.

SECTION 5

RESULTS AND DISCUSSION

The results obtained from these studies are presented in the following terms:

- Boiler Operating Conditions for Test
- Coal Analysis
- Characterization of Waste Streams
- Mass Balance

BOILER OPERATING CONDITIONS FOR TEST

During each test, all data on the unit operating conditions were obtained from the control room instrumentation on an hourly basis and were averaged for each parameter (Table 5). It can be seen that the unit was operated at essentially constant conditions with relatively minor variations in operating conditions. Initial study plans called for conducting the tests under various boiler operating conditions; but cracks in the turbine spindle, discovered during annual outage, necessitated operating the boiler at "near full" load during the entire 2-week testing period.

COAL ANALYSIS

Since the composition of coal varies greatly from source to source and even within a single source (coal bed), the composition of ash and stack emissions can also vary greatly. Coal burned during the test period was mined from the coal fields of western Kentucky. The coal consisted of carbonaceous matter and a mixture of various minerals (shales, clays, sulfides, and carbonates).

Proximate analysis of the whole coal and pulverized coal samples is summarized in Table 6. The results were essentially the same for both coal samples. Ultimate analysis of the pulverized coal is summarized in Table 7. In the ultimate analysis, oxygen is calculated by subtracting the sum of the percentages of moisture, ash content, carbon, hydrogen, and nitrogen from 100 percent.

The ash from the proximate analysis was analyzed for nine major elements and the results are given as oxides of the elements in Table 8. The values for all oxides, except SiO_2, were obtained using standard analytical procedures. It was assumed that the nine oxides in Table 8 comprised 99.5 percent of the total residue. Since SiO_2 is extremely difficult to measure chemically, SiO_2 was determined by subtracting the sum of the other eight oxides from 99.5 percent.

The coal samples were analyzed for the trace element listed in Table 3. These data were combined with the proximate and ultimate analysis to provide an additional check on the balance of elements in the coal. The sum of the

TABLE 5. BOILER OPERATING CONDITIONS FOR TEST

(AVERAGE VALUES)

	Test							
	1	2	3	4	5	6	7	8
Load (MW)	183	179	188	181	182	184	188	183
Bar. Pressure (in. of Hg)	29.71	29.79	29.76	29.63	29.68	29.73	29.70	29.74
Air Flow 10^6 (lb/h)	1.28	1.27	1.35	1.25	1.27	1.27	1.30	1.27
Steam Flow 10^6 (lb/h)	1.28	1.13	1.34	1.28	1.30	1.31	1.32	1.29
Pulverizer A (Amps)	49	47	12.3*	49	50	46	48	49
B	40	32*	32*	0*	0*	29*	41	0*
C	0	32*	45	46	45	44	48	48
D	47	32*	50	47	44	41	46	41
E	44	43	46	45	49	49	0*	45
F	45	48	46	44	48	42	45	46
FD Fan A (Amps)	55	56	57	55	55	56	57	56
ID Fan A	152	148	159	153	155	154	158	156
FD Fan B	60	60	60	58	58	58	60	60
ID Fan B	161	161	170	161	158	155	163	161
Furnace Draft A (in. of H_2O)	-.43	-.59	-.65	-.46	-.54	-.51	-.54	-.58
Furnace Draft B	-.45	-.63	-.55	-.46	-.54	-.50	-.54	-.58
Air Heater Diff. A (in. of H_2O)	3.06	3.1	3.3	3.0	3.1	3.0	3.3	3.1
B	3.04	3.0	3.2	3.0	3.0	2.8	3.4	3.3
Gas Leaving Air Heater A (°F)	342	344	345	341	344	344	344	343
Gas Leaving Air Heater B (°F)	343	345	340	352	348	345	344	340

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*Indicates pulverizer was off for one or more sampling periods.

TABLE 6. PROXIMATE ANALYSIS OF WHOLE COAL

Test	1	2	3	4	5	6	7	8	Avg.
% Moisture	7.9	5.6	5.5	5.4	6.4	7.0	7.4	5.8	6.4
% Ash	15.5	16.4	14.3	15.0	16.4	15.5	15.6	15.7	15.6
% Volatile Matter	37.4	36.8	38.5	37.6	37.0	37.5	37.8	37.7	37.5
% Carbon	47.1	46.8	47.2	47.4	46.6	47.0	46.6	46.6	46.9
% Sulfur	4.2	4.0	3.8	4.0	5.2	4.5	4.2	3.9	4.2
Btu/lb as Received	11349	11590	11922	11813	11488	11536	11456	11636	11599
Btu/lb Dry	12323	12278	12616	12487	12273	12404	12372	12352	12388
Btu/lb A & MF	14584	14686	14719	14685	14677	14675	14659	14651	14667

PROXIMATE ANALYSIS OF PULVERIZED COAL

Test	1	2	3	4	5	6	7	8	Avg.
% Moisture	1.1	2.6	2.3	2.1	2.8	2.6	2.6	2.3	2.3
% Ash	15.8	15.4	13.8	14.8	15.1	14.8	16.6	16.7	15.4
% Volatile Matter	37.2	37.7	38.4	37.8	37.6	37.4	37.7	38.1	37.7
% Carbon	47.0	46.9	47.8	47.4	47.3	47.8	45.7	45.2	46.9
% Sulfur	3.8	3.9	3.6	3.9	4.1	3.9	3.9	3.9	3.9
Btu/lb as Received									
Btu/lb Dry	12296	12300	12550	12472	12488	12521	12150	12142	12365
Btu/lb A & MF	14602	14539	14562	14640	14712	14693	14574	14574	14612

TABLE 7. ULTIMATE ANALYSIS OF PULVERIZED COAL

Test	1	2	3	4	5	6	7	8	Avg.
% Carbon	67.7	68.2	69.5	68.9	68.9	69.3	67.1	67.1	68.3
% Hydrogen	4.8	4.8	4.8	4.8	4.8	4.8	4.7	4.7	4.8
% Nitrogen	1.5	1.5	1.6	1.5	1.5	1.5	1.5	1.5	1.5
% Oxygen*	6.4	6.2	6.6	6.1	5.6	5.7	6.2	6.1	6.1

*Note: Percent oxygen is obtained by difference and was not directly analyzed.

TABLE 8. MAJOR ELEMENTS (GIVEN AS OXIDES) OF ASH PRODUCED IN THE LABORATORY BY FIRING COAL AT APPROXIMATELY 800°F

(Percent)

Test	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_2	Na_2O	K_2O	TiO_2	Total
1	48.7	17.9	20.0	4.8	1.1	2.9	0.6	2.6	0.9	99.5
2	48.8	17.6	20.9	4.5	1.1	2.6	0.6	2.5	0.9	99.5
3	49.7	18.3	20.3	4.0	1.0	2.3	0.5	2.5	0.9	99.5
4	49.1	17.8	21.4	3.9	1.1	2.2	0.6	2.5	0.9	99.5
5	49.1	17.1	21.8	4.2	1.1	2.4	0.6	2.4	0.8	99.5
6	49.1	17.1	21.4	4.3	1.1	2.7	0.6	2.4	0.8	99.5
7	50.8	17.7	19.5	4.3	1.1	1.9	0.6	2.7	0.9	99.5
8	50.3	17.3	20.2	4.5	1.1	2.0	0.5	2.7	0.9	99.5

TABLE 9. CHEMICAL BALANCE AROUND THE PULVERIZED COAL USING TRACE ELEMENT ANALYSIS AND ULTIMATE ANALYSIS OF COAL

	Test							
	1	2	3	4	5	6	7	8
Sum of 27 Element Concentrations (%) in Pulverized Coal*	12.14	10.96	10.26	10.42	11.70	11.12	11.25	10.99
Carbon**	67.7	68.2	69.5	68.9	68.9	69.3	67.1	67.1
Hydrogen**	4.8	4.8	4.8	4.8	4.8	4.8	4.7	4.7
Nitrogen**	1.5	1.5	1.6	1.5	1.5	1.5	1.5	1.5
Oxygen**	6.4	6.2	6.6	6.1	5.6	5.7	6.2	6.1
Moisture**	1.1	2.6	2.3	2.1	3.8	2.6	2.6	2.3
Total	93.64	94.26	95.06	93.82	95.30	95.02	93.35	92.69

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*Sum of 27 element concentrations in pulverized coal samples.
**From ultimate coal analyses (Table 7).

trace elements, carbon, hydrogen, nitrogen, oxygen, and moisture is shown to represent 94 percent of the total coal (Table 9).

The results of the trace element analysis of coal are reported in Table 10. The three predominate elements in coal, excluding sulfur, are silicon, aluminum, and iron; these 3 elements comprise approximately 86 percent of the total mass of elements. Calcium, magnesium, potassium, sodium, chlorine, oxygen, and titanium comprise an additional 13.2 percent. The remaining trace elements provide less than 1 percent of the total mass of elements.

CHARACTERIZATION OF WASTE STREAMS

The characteristics of each trace element in coal cause each element to be dispersed to the various ash streams or to volatilize and be released to the atmosphere in the stack gas following combustion. The primary objective of this effort was to simply characterize the waste streams from a utility boiler. For convenience in presenting the data and discussion of the results, the elements have been divided into the following five groups:

Group A - Alkali Earth and Alkali Metals (Ba, Ca, Mg, K, Na)

Group B - Halogens (Cl, F)

Group C - Volatiles (those elements most likely to form volatile combustion products) (Sb, As, Be, B, Hg, Se, S)

Group D - Refractories (those elements most likely to form highly refractory oxides on combustion) (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Si, Ti, V, Zn)

Group E - Heavy Metals (Pb)

Coal and Ash

The concentration of a number of trace elements was investigated in each of the daily test samples of pulverized coal, pyrites, and the ash samples. The results are reported in Tables 10 and 11. As one might anticipate, the major constituents of the ash were iron, aluminum, and silicon. Following these three major constituents in order of abundance were calcium, potassium, magnesium, sulfur, titanium, and sodium.

Ash Sluice Water

To provide background water quality data, inflow water samples were collected during each daily test. All bottom ash samples and eight ESP fly ash samples were collected as slurry as they were being sluiced to the ash pond. After a 45-minute settling period, a water sample was siphoned from the top of the samples. Following the 14-hour settling

TABLE 10. TRACE ELEMENT CONCENTRATION IN COAL, PYRITES, BOTTOM ASH, AND MECHANICAL COLLECTOR ASH (μg/g)

	Group A					Group B		Group C							Group D												Group E
Test	Ba	Ca	Mg	K	Na	Cl	F	Sb	As	Be	B	Hg	Se	S	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Si	Ti	V	Zn	Pb
WHOLE COAL																											
1	120	5040	735	1800	600	1400	50	1.9	15	1.1	-	0.32	2.9	-	16000	<5	<5	17.4	8.7	17900	41.0	8.5	30900	638	52.6	2045	17.7
2	100	6420	937	2300	650	1800	60	2.3	15	1.3	-	0.27	3.3	-	16000	<5	<5	20.2	10.3	22800	53.8	9.4	31100	835	64.0	3065	21.8
3	100	4600	655	1600	500	1600	60	2.4	8	1.1	-	0.25	2.7	-	14000	<5	<5	14.7	8.0	16600	34.8	7.3	25300	658	59.0	3872	15.4
4	<50	4120	780	1900	650	1800	10	2.5	10	1.3	-	0.27	3.4	-	14000	<5	<5	19.8	9.6	18200	38.8	8.1	27100	700	75.5	685	18.0
5	<50	4090	751	2100	750	1800	100	2.1	17	1.3	-	0.22	2.8	-	14000	<5	<5	19.1	9.9	24000	42.7	11.2	30200	703	74.2	1707	24.1
6	<50	4570	773	2100	650	1800	80	1.9	11	1.2	-	0.23	2.9	-	11000	<5	<5	18.4	5.9	20700	46.4	12.0	25200	707	68.2	2167	28.0
7	100	3990	794	2000	600	1300	160	2.1	9	1.6	-	0.23	3.0	-	14000	<5	<5	20.6	5.4	20200	34.2	8.7	29800	711	94.1	4693	21.6
8	270	5380	998	1700	650	1500	200	1.8	9	1.3	-	0.28	3.4	-	16000	<5	<5	18.9	6.7	21100	41.4	11.0	33900	677	66.3	1970	28.9
PULVERIZED COAL																											
1	180	4220	941	3530	417	1800	41	2.0	12	1.40	90	0.15	4.0	35000	17200	1	25	25.7	18.6	22500	55.1	18	34300	731	76.2	54.0	18
2	95	3370	748	3000	375	1900	10	2.1	16	1.01	80	<0.10	4.7	34000	15000	<1	36	22.9	12.5	23000	47.1	17	27000	641	69.1	45.1	19
3	54	2870	676	2640	319	1600	36	1.9	24	1.30	100	<0.10	3.7	34000	14700	1	<3	21.6	11.0	20600	37.7	14	24000	595	68.1	38.5	14
4	70	2640	708	2910	373	2000	<5	2.9	20	1.15	90	0.10	4.7	36000	14500	<1	18	20.5	10.8	21100	38.3	15	22800	630	69.5	41.1	16
5	85	2890	661	2810	425	2000	46	2.4	19	1.17	90	0.12	4.4	37000	14000	<1	18	22.5	11.6	24000	47.2	17	32000	601	75.6	45.4	19
6	100	2810	620	2460	275	1800	16	2.3	16	0.94	90	0.12	4.5	35000	14500	<1	10	16.3	10.1	27100	41.4	15	25500	490	57.2	39.1	20
7	40	4160	1060	3600	275	1600	22	2.5	19	1.59	90	0.10	5.5	35000	15000	<1	17	29.6	13.0	24000	49.8	14	26500	728	76.1	54.4	17
8	69	4040	1050	3770	319	1600	40	2.2	21	1.43	90	0.13	3.1	37000	15200	<1	15	24.3	12.8	22500	46.2	15	23000	719	77.9	36.8	43
PYRITE																											
1	985	9270	1400	3960	466	53	56	2.6	120	1.09	50	0.68	7.1	262000	19100	<1	49	38.9	29.7	185000	136	28	29900	735	66.6	279	102
2	735	8280	1810	5530	457	10	28	3.0	140	1.88	50	0.77	6.5	164000	18800	<1	52	60.2	41.4	240000	142	84	34600	1070	141	255	166
3	465	6650	1500	4260	275	45	56	1.5	110	1.01	50	0.95	7.4	404000	19500	<1	33	36.9	40.5	265000	120	71	30500	857	72.6	142	222
4	180	4670	1090	3350	325	37	38	3.4	110	0.89	50	0.75	10.0	102000	18000	<1	38	53.3	26.4	210000	95.5	51	31000	686	77.1	85.6	129
5	185	6520	1470	3960	325	45	50	1.8	77	1.12	40	0.85	10.0	301000	17500	2	44	53.1	36.8	251000	155	93	31500	801	74.9	101	199
6	605	8370	1740	5090	310	62	50	2.7	72	1.72	50	0.58	9.1	341000	15500	2	35	57.4	31.3	215000	397	57	27500	1050	114	193	177
7	270	9240	1850	5260	564	67	56	2.3	55	1.33	50	1.0	21.0	149000	19100	<1	44	41.5	28.2	230000	182	46	40700	975	88.3	267	162
8	200	8700	1730	5600	838	34	80	2.2	70	1.18	50	1.1	17.0	318000	29400	<1	44	55.1	32.6	205000	152	63	65700	994	66.0	126	156
BOTTOM ASH																											
1	935	30900	6670	21200	2620	17	<5	4.2	4	8.00	230	<0.10	0.5	3600	95000	<1	40	164	73.3	190000	597	100	159000	6960	463	258	95
2	1140	26300	5580	18200	2720	52	<5	3.2	5	6.96	220	<0.10	0.4	2000	98000	<1	49	152	67.4	195000	352	100	136000	4000	428	213	92
3	715	19900	4050	15700	2580	26	<5	4.3	8	6.37	250	<0.10	0.9	5200	90000	<1	35	141	58.3	200000	255	94	134000	3610	377	138	73
4	780	31700	5650	16500	2430	75	<5	5.0	15	6.88	180	<0.10	1.0	3600	76800	<1	51	139	69.9	183000	311	100	159000	3850	429	234	111
5	710	22500	5000	16700	2760	39	<5	4.5	12	6.61	250	0.10	0.7	5600	81800	<1	41	154	68.8	192000	373	110	151000	4020	437	224	101
6	1050	20200	4740	16200	2480	17	<5	3.7	7	6.14	200	<0.10	0.7	3200	83300	<1	52	206	64.3	227000	342	93	132000	3550	426	177	93
7	855	14700	3410	11900	2920	28	<5	5.2	8	3.66	220	<0.10	0.5	2200	85000	<1	39	120	38.4	195000	181	100	152000	2250	214	107	84
8	550	18700	4360	18500	2920	26	<5	3.0	8	5.42	250	<0.10	0.6	3100	88600	<1	45	115	55.1	172000	224	114	142000	3640	316	122	81
MECHANICAL COLLECTOR																											
1	960	33000	4610	14400	2020	46	<5	6.5	14	5.29	180	<0.10	2.0	5200	70000	<1	42	123	70.6	260000	377	107	106000	3250	400	160	97
2	1230	33900	4650	13900	2220	38	<5	4.3	18	5.69	210	<0.10	2.4	5600	75000	<1	66	135	71.2	260000	366	108	112000	3350	395	200	118
5	1060	16200	2140	10000	2020	37	<5	2.7	14	4.10	200	<0.10	2.5	4700	75000	<1	56	79.9	43.1	265000	237	103	124000	2590	297	136	96
6	1350	24600	4810	13100	2180	40	<5	3.3	15	6.24	210	<0.10	2.1	4400	75000	<1	51	155	78.7	265000	647	115	124000	3390	428	232	102
7	935	36800	4800	14100	2120	36	<5	5.2	16	5.70	210	<0.10	2.0	4100	75000	<1	56	128	63.5	290000	420	108	112000	3290	383	163	98
8	1480	37500	4850	15400	2080	36	<5	4.3	12	5.48	220	<0.10	2.8	4300	75000	<1	62	130	71.3	265000	354	84	123000	3470	374	170	95

TABLE 11. TRACE ELEMENT CONCENTRATION IN ESP INLET PARTICULATE, ESP HOPPER ASH AND ESP OUTLET PARTICULATE (μg/l)

	Group A					Group B		Group C							Group D												Group E
Test	Ba	Ca	Mg	K	Na	Cl	F	Sb	As	Be	B	Hg	Se	S	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Si	Ti	V	Zn	Pb
ELECTROSTATIC PRECIPITATOR INLET																											
1	1300	30400	5970	16100	4600	6900	420	18	83	8.9	-	0.38	19	-	100000	15	44	567	82	111000	468	137	188000	5340	477	579	84
2	1010	26700	5725	17800	4500	4550	400	24	90	10.2	-	0.63	14	-	100000	14	44	739	100	116500	414	196	190500	5490	548	632	78
3	710	22800	5150	20300	4600	2800	260	17	99	10.4	-	0.75	17	-	100000	13	41	475	92	113000	343	204	191000	5280	557	564	61
4	810	23100	5170	10400	4400	2800	245	12	82	9.4	-	0.38	20	-	100000	17	46	366	88	108000	340	138	191000	4950	526	633	100
5	980	26500	5950	22100	4800	5100	310	19	100	10.7	-	0.58	19	-	97000	13	47	507	99	113000	470	168	192000	5650	575	733	113
6	980	24700	5670	19800	4900	2900	245	31	100	10.7	-	0.52	19	-	100000	13	42	515	92	108000	421	167	192000	5240	612	666	96
7	590	18900	4810	17800	4200	2500	230	15	79	10.3	-	0.60	15	-	100000	11	46	606	83	98100	276	189	195000	5300	483	449	45
8	550	24100	5840	23600	4500	3800	300	19	81	10.4	-	0.67	19	-	100000	14	46	722	86	91300	313	221	204000	5580	524	545	36
ELECTROSTATIC PRECIPITATOR HOPPER ("B" SIDE)																											
1	1100	40800	6990	17100	3800	100	70	10	25	11.4	-	0.22	4.0	-	91000	9	24	152	79	151000	424	85	201000	5990	541	556	75
2	1045	40950	6390	17450	3750	200	75	13	32	9.0	-	0.69	3.8	-	96500	7	28	144	76	148000	423	83	191000	5640	494	515	82
3	670	33500	5820	17900	4000	100	100	15	13	9.4	-	0.10	6.0	-	96000	5	33	139	74	150000	350	80	189000	5430	489	428	70
4	660	35600	6190	18300	4200	100	70	18	78	8.6	-	0.10	3.3	-	99000	5	35	135	71	155000	372	76	195000	5480	481	443	62
5	1000	32600	5970	19100	3900	100	10	10	33	9.4	-	0.90	4.0	-	100000	6	60	142	73	153000	384	84	196000	5520	580	478	75
6	980	35400	5640	15100	4400	100	70	15	34	9.4	-	0.48	5.0	-	94000	5	43	200	68	149000	433	72	201000	4950	531	506	75
7	830	31200	5600	12300	4100	100	50	14	180	10.3	-	0.10	4.7	-	96000	11	56	94	46	109000	328	53	195000	3020	328	381	66
8	720	37800	7020	18200	4100	100	20	16	64	10.6	-	0.88	6.3	-	96000	5	62	141	73	149000	342	78	199000	6320	522	454	81
ELECTROSTATIC PRECIPITATOR HOPPER (ENTIRE UNIT)																											
1	1180	26900	6160	22200	2820	37	<5	11	45	8.48	500	<0.10	3.1	5700	100000	2	15	173	90.9	130000	338	100	138000	4770	472	367	140
2	1080	27900	6230	22300	3420	47	40	20	57	8.80	480	<0.10	3.4	5600	105000	3	44	167	105	135000	356	110	141000	4750	505	410	140
3	640	25700	5760	21200	3320	22	<5	16	78	9.52	480	<0.10	4.2	4900	90000	4	48	151	86.6	150000	304	106	144000	4400	508	462	135
4	885	21000	5700	21200	3520	50	<5	12	60	8.42	470	<0.10	3.5	4500	100000	4	50	163	86.4	150000	290	97	150000	4760	508	373	120
5	935	20500	4950	20500	3680	43	<5	12	80	7.66	500	<0.10	4.1	5100	100000	8	44	150	79.5	155000	341	104	138000	4260	449	337	150
6	1000	31300	6690	20800	3280	37	<5	14	75	9.75	450	0.17	4.2	5300	90000	2	36	179	101	169000	439	107	164000	4800	578	542	152
7	640	25250	5880	21500	3480	27	<5	7.3	64	9.06	450	<0.10	3.7	4600	100000	4	30	151	83.0	150000	295	88	150000	4410	459	376	114
8	635	24000	5870	23200	3480	96	<5	12	57	8.07	440	0.17	-4.5	4900	95000	2	50	144	80.0	150000	264	109	138000	4460	441	316	127
ELECTROSTATIC PRECIPITATOR OUTLET																											
1	168	7750	2100	2750	-	2715	155	60	366	2.5	-	1.16	3.8	-	13600	53	829	28200	269	190000	3600	8540	-	628	171	476	41
2	51	2815	783	2280	-	3418	160	106	726	1.4	-	5.74	1.8	-	4670	37	1100	39050	228	220000	5025	8890	-	227	122	597	42
3	84	5930	1200	1590	-	29567	527	65	550	1.8	-	16.0	1.5	-	7400	86	491	22400	643	92000	2460	9660	-	266	121	781	74
4	40	2890	802	1190	-	14083	159	90	1295	1.3	-	0.54	5.5	-	4430	41	1200	31600	300	210000	5340	13400	-	146	125	692	56
5	21	2610	352	978	-	3339	14[illegible]	114	534	1.1	-	0.85	7.8	-	1430	30	1000	47400	390	200000	5430	21100	-	66	123	960	38
6	79	6240	1620	5120	-	4493	25[illegible]	119	1005	3.0	-	0.78	6.4	-	10200	99	608	39200	1200	100000	2080	17840	-	471	210	1540	95
7	26	6500	1220	3500	-	36223	289	101	660	3.2	-	17.0	22.9	-	11200	56	445	35600	1600	77000	1630	19300	-	514	203	959	85
8	88	6200	1530	3940	-	3749	214	40	938	2.4	-	13.6	22.5	-	12500	45	413	12900	495	77000	1120	6190	-	618	152	810	59

period all the water was siphoned from the settled solids, the decanted water volume was measured, and a sample was retained for analysis. Results of the field and laboratory water analyses are reported in Tables 12, 13, and 14.

This sampling scheme was used to evaluate the leaching characteristics of the major and minor trace elements in ash. Bottom ash (Table 12) had little effect on the raw sluice water trace element concentration (Table 13). Increases in the Ca and $SO_4^=$ content were most noticeable with minimum increases in Cl, F, As, B, Al, and Si. During the bottom ash sluicing, Zn and Cu appeared to have been partially removed from the dissolved portion of the sluice water.

The effect of ESP ash (Table 13) on the raw sluice water dissolved trace elements was generally the same as the effect of the bottom ash. Constituents showing the largest increases were Ca, K, Na, Al, and $SO_4^=$, Cl, F, As, B, Se, Al, and Cr showed slight increases. Mg, Cu, and Si appear to have been removed from the dissolved portion of the sluice water during the fly ash sluicing.

It should be noted that there were essentially no differences between the respective 45-minute and 14-hour supernatant samples for the concentrations of Ca, Mg, $SO_4^=$, Si, and Hg, suggesting that any chemical reactions between the ash and the dissolved portion of the 14-hour sluice water sample occurred during the sluicing operation (~ 7-minute flow time) for the elements measured (see Table 12).

The field analysis of sluice waters (Table 14) shows similar results in that the respective 45-minute and 14-hour samples displayed essentially the same characteristics. The ESP ash had a much more pronounced effect on the sluice water quality parameters determined in the field than did the bottom ash.

Fine Particulate Characterization

Physical Characterization

The size distribution, number, and mass concentration of the fine particulates were determined for particles between 0.005 and 10 µm by using four different instruments. Aerodynamic cascade impactors measured particles with aerodynamic diameters between 0.5 to 10 µm. Particles having diameters between 0.3 to 1.5 µm were counted with an optical counter. Smaller particles having nuclei-size particles were counted using the diffusion principle with a condensation nuclei counter. Size fraction measurement, particle color, and aspect ratio from the aerodynamic cascade impactors were confirmed by Walter C. McCrone Associates, Inc., with the use of a light transmission microscope and a scanning electron microscope.

TABLE 12. TRACE ELEMENT CONCENTRATION IN BOTTOM ASH AND ELECTROSTATIC PRECIPITATION SLUICE WATER SAMPLES (mg/l)

	Group A					Group B		Group C							Group D													Group E
Test	Ba	Ca	Mg	K	Na	Cl	F	Sb	As	Be	B	Hg	Se	SO_4	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Si	Ti	V	An	Pb
BOTTOM ASH SLUICE WATER (DISSOLVED) - SETTLING TIME - 14 H																											
1	<0.1	37	2.9	1.9	5.4	13	0.10	<0.1	0.016	<0.01	0.30	<0.0002	<0.001	71	0.5	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	3.6	<1	0.4	0.01	<0.010
2	<0.1	38	3.4	1.8	5.5	7	0.08	<0.1	0.013	<0.01	0.20	<0.0002	<0.001	57	0.3	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	3.1	<1	0.2	0.01	<0.010
3	<0.1	75	3.5	1.9	5.4	8	0.13	<0.1	0.009	<0.01	0.20	<0.0002	0.002	130	0.3	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	2.9	<1	<0.1	0.01	<0.010
4	<0.1	65	3.6	1.8	5.6	10	0.14	<0.1	0.009	<0.01	0.30	<0.0002	0.003	120	0.3	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	2.7	<1	<0.1	0.01	<0.010
5	<0.1	28	3.6	1.8	5.9	13	0.09	<0.1	0.009	<0.01	0.16	<0.0002	<0.001	43	0.2	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	2.6	<1	<0.1	0.02	<0.010
6	<0.1	34	3.3	1.8	5.6	11	0.08	<0.1	0.009	<0.01	0.15	<0.0002	<0.001	76	0.3	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	3.1	<1	0.2	0.01	0.010
7	<0.1	33	3.2	1.7	5.7	14	0.09	<0.1	0.009	<0.01	0.25	<0.0002	<0.001	76	0.4	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	3.2	<1	<0.1	0.01	<0.010
8	<0.1	29	3.0	1.9	6.2	11	0.07	<0.1	0.011	<0.01	0.28	<0.0002	<0.001	82	0.3	<0.001	<0.005	<0.005	<0.01	<0.05	<0.01	<0.05	3.2	<1	<0.1	0.01	<0.010
BOTTOM ASH SLUICE WATER (DISSOLVED) - SETTLING TIME - 45 MIN																											
1		33	2.9									0.0002		74									3.5				
2		35	3.4									<0.0002		51									2.9				
3		64	3.5									<0.0002		110									2.7				
4		57	3.6									<0.0002		74									2.6				
5		26	3.6									<0.0002		40									2.4				
6		32	3.3									<0.0002		63									3.0				
7		32	3.2									<0.0002		62									2.9				
8		27	3.1									<0.0002		68									3.0				
ELECTROSTATIC PRECIPITATOR SLUICE WATER (DISSOLVED) - SETTLING TIME - 14 H																											
1	0.3	660	0.02	23	20	13	0.53	<0.1	0.006	<0.01	8.2	<0.0002	0.033	490	0.4	<0.001	<0.005	0.098	0.01	<0.05	<0.01	<0.05	0.56	<1	<0.1	0.06	0.012
2	0.3	520	0.02	21	18	11	0.46	<0.1	<0.002	<0.01	8.2	<0.0002	0.040	580	1.2	<0.001	<0.005	0.060	0.01	<0.05	<0.01	<0.05	0.71	<1	<0.1	0.03	0.015
3	<0.1	440	0.02	23	19	11	0.44	<0.1	0.005	<0.01	8.0	<0.0002	0.040	490	3.6	<0.001	<0.005	0.063	<0.01	<0.05	<0.01	<0.05	0.84	<1	0.5	0.03	0.011
4	<0.1	410	0.03	21	19	12	0.42	<0.1	<0.002	<0.01	7.0	<0.0002	0.028	440	4.0	<0.001	<0.005	0.072	<0.01	<0.05	<0.01	<0.05	0.98	<1	0.1	0.02	<0.010
5	0.3	460	0.02	21	20	12	0.40	<0.1	0.009	<0.01	7.0	<0.0002	0.023	560	2.8	<0.001	<0.005	0.075	<0.01	<0.05	<0.01	<0.05	0.75	<1	<0.1	0.03	<0.010
6	<0.1	420	0.03	20	19	13	0.49	<0.1	<0.002	<0.01	5.5	<0.0002	0.050	520	3.9	<0.001	<0.005	0.079	<0.01	<0.05	<0.01	<0.05	0.98	<1	0.4	0.02	<0.010
7	0.2	490	0.02	21	18	10	0.53	0.2	0.002	<0.01	4.0	<0.0002	0.042	620	1.8	<0.001	<0.005	0.068	<0.01	<0.05	<0.01	<0.05	0.75	<1	0.2	0.02	<0.010
8	0.4	510	0.02	23	19	10	0.61	0.2	0.008	<0.01	7.0	<0.0002	0.058	740	1.4	<0.001	<0.005	0.060	<0.01	<0.05	<0.01	<0.05	0.93	<1	0.2	0.02	<0.010
ELECTROSTATIC PRECIPITATOR SLUICE WATER (DISSOLVED) - SETTLING TIME - 45 MIN																											
1		640	0.01									<0.0002		590									0.71				
2		530	0.02									<0.0002		460									0.84				
3		430	0.02									<0.0002		500									0.79				
4		390	0.03									<0.0002		420									0.89				
5		450	0.02									<0.0002		640									0.71				
6		400	0.04									<0.0002		550									0.71				
7		480	0.03									<0.0002		500									0.47				
8		510	0.03									<0.0002		480									0.61				

TABLE 13. TRACE ELEMENT CONCENTRATION IN INFLOW WATER SAMPLES (mg/l)

	Group A					Group B		Group C							Group D												Group E	
Test	Ba	Ca	Mg	K	Na	Cl	F	Sb	As	Be	B	Hg	Se	SO_4	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Si	Ti	V	Zn	Pb	SS
														INFLOW WATER (SUSPENDED)														
1	<0.002	0.14	0.04	0.04	0.01	7*	0.08*	0.002	-	<0.001	0.04*	-	-	17*	0.38	0.001	0.0003	0.004	0.05	1.4	0.08	0.002	-	-	<0.002	0.02	0.011	13
2	<0.002	0.13	0.06	0.04	0.01	7*	0.06*	0.005	-	<0.001	0.04*	-	-	15*	0.57	0.001	0.0005	0.006	0.08	0.68	0.10	0.002	-	-	0.003	0.02	0.011	10
3	<0.002	0.18	0.08	0.06	0.02	8*	0.06*	0.005	-	<0.001	0.06*	-	-	18*	0.59	0.002	0.0008	0.008	0.10	0.97	0.18	0.002	-	-	<0.002	0.03	0.018	11
4	<0.002	0.11	0.05	0.05	0.01	7*	0.06*	0.004	-	<0.001	0.09*	-	-	14*	0.49	0.002	0.0003	0.004	0.06	0.47	0.07	<0.001	-	-	<0.002	0.02	0.007	9
5	<0.002	0.10	0.04	0.03	0.01	7*	0.06*	0.002	-	<0.001	0.06*	-	-	9*	0.26	<0.001	0.0003	0.003	0.02	0.23	0.04	<0.001	-	-	<0.002	0.02	0.003	2
6	<0.002	0.15	0.08	0.05	0.04	8*	0.06*	0.004	-	<0.001	0.11*	-	-	12*	0.65	0.002	0.0005	0.003	0.12	0.80	0.11	0.002	-	-	<0.002	0.02	0.014	10
7	<0.002	0.18	0.05	0.06	0.06	8*	0.06*	<0.002	-	<0.001	0.08*	-	-	10*	0.41	<0.001	0.0003	0.005	0.02	0.33	0.06	<0.001	-	-	<0.002	0.01	0.004	3
8	<0.002	0.15	0.06	0.04	0.06	7*	0.06*	0.005	-	<0.001	0.04*	-	-	11*	0.41	<0.001	0.0002	0.004	0.04	0.33	0.07	<0.001	-	-	<0.002	0.01	0.004	3
														INFLOW WATER (DISSOLVED)														TDS
1	<0.1	19	3.6	1.4	5.3	7	0.06	<0.1	<0.002	<0.01	0.03	<0.0002	<0.001	17	<0.1	0.002	<0.005	<0.005	0.03	<0.05	0.02	<0.05	2.1	<1	<0.1	0.11	<0.010	93
2	<0.1	18	3.6	1.3	5.0	7	0.06	<0.1	<0.002	<0.01	0.04	<0.0002	<0.001	15	<0.1	<0.001	<0.005	<0.005	0.02	0.05	0.02	<0.05	2.1	<1	0.2	0.02	<0.010	80
3	<0.1	18	3.6	1.3	5.1	8	0.06	<0.1	<0.002	<0.01	0.06	<0.0002	<0.001	18	<0.1	<0.001	<0.005	<0.005	0.03	<0.05	0.01	<0.05	2.1	<1	<0.1	0.04	<0.010	81
4	<0.1	17	3.6	1.3	5.1	7	0.06	<0.1	<0.002	<0.01	0.06	<0.0002	<0.001	14	<0.1	<0.001	<0.005	<0.005	0.03	<0.05	<0.01	<0.05	2.1	<1	<0.1	0.03	<0.010	89
5	<0.1	17	3.6	1.4	5.6	7	0.06	<0.1	<0.002	<0.01	0.06	<0.0002	<0.001	9	<0.1	<0.001	<0.005	<0.005	0.02	<0.05	<0.01	<0.05	2.1	<1	<0.1	0.03	<0.010	42
6	<0.1	17	3.6	1.3	5.3	8	0.06	<0.1	<0.002	<0.01	0.11	<0.0002	<0.001	12	<0.1	<0.0	0.005	<0.005	0.03	<0.05	<0.01	<0.05	2.1	<1	<0.1	0.04	<0.010	50
7	<0.1	17	3.6	1.2	5.3	8	0.06	<0.1	<0.002	<0.01	0.08	<0.0002	<0.001	10	<0.1	<0.0	.005	<0.005	0.02	<0.05	<0.01	<0.05	2.1	<1	<0.1	0.02	<0.010	83
8	<0.1	17	3.6	1.3	5.5	7	0.06	<0.1	<0.002	<0.01	0.04	<0.0002	<0.001	11	<0.1	0.0	<0.005	<0.005	0.03	<0.05	<0.01	<0.05	2.1	<1	<0.1	0.01	F0.010	43

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*Questionable data

TABLE 14. FIELD ANALYSIS OF ASH SLUICE WATER SAMPLES INFLOW DAILY COMPOSITE

Test	pH (units)	Alkalinity as $CaCO_3$ Phen. (mg/l)	Alkalinity as $CaCO_3$ Total (mg/l)	ORP (mV)	Conductivity (μmhos)
1	7.60	0	48	265	172
2	7.35	0	45	260	175
3	7.80	0	45	240	155
4	7.7	0	45	280	163
5	7.9	0	45	340	165
6	8.3	0	45	260	170
7	8.0	0	45	280	170
8	7.9	0	45	320	160
Avg.	7.8	0	45	281	166

BOTTOM ASH SLUICE WATER

(Settling Time - 45 min)

Test	pH (units)	Alkalinity as $CaCO_3$ Phen. (mg/l)	Alkalinity as $CaCO_3$ Total (mg/l)	ORP (mV)	Conductivity (μmhos)
1	9.3	14	44	215	285
2	9.0	9	60	160	230
3	8.9	11	65	120	425
4	8.8	10	67	120	350
5	8.8	6	53	245	220
6	9.2	10	53	220	260
7	9.6	12	47	190	290
8	9.4	12	42	210	215
Avg.	9.1	10	54	185	284

(Settling Time - 14 h)

Test	pH (units)	Alkalinity as $CaCO_3$ Phen. (mg/l)	Alkalinity as $CaCO_3$ Total (mg/l)	ORP (mV)	Conductivity (μmhos)
1	9.5	16	45	150	250
2	9.0	9	72	180	300
3	8.9		56	160	272
4	8.9	0	41	335	490
5	8.9	6	52	240	215
6	9.2	8	50	245	260
7	9.3	10	43	236	256
8	9.6	10	35	245	230
Avg.	9.2	8	49	224	284

TABLE 14. (Continued)

ELECTROSTATIC PRECIPITATOR SLUICE WATER

(Settling Time - 45 min)

Test	pH (units)	Alkalinity as $CaCO_3$ Phen. (mg/l)	Alkalinity as $CaCO_3$ Total (mg/l)	ORP (mV)	Conductivity (μmhos)
1	11.6	1020	1084	-	4100
2	11.5	772	805	15	4000
3	11.6	521	613	25	2600
4	11.3	456	506	40	2750
5	11.6	581	633	95	3250
6	11.8	460	509	85	2700
7	11.8	676	725	90	3600
8	11.8	714	765	85	3400
Avg.	11.5	650	705	62	3300

(Settling Time - 14 h)

Test	pH (units)	Alkalinity as $CaCO_3$ Phen. (mg/l)	Alkalinity as $CaCO_3$ Total (mg/l)	ORP (mV)	Conductivity (μmhos)
1	11.9	1064	1101	10	4000
2	11.9	750	792	10	4000
3	11.8	545	595	5	2600
4	11.5	-	-	-	-
5	12.0	607	670	90	3450
6	12.2	530	573	85	3100
7	12.4	674	722	55	3200
8	12.6	757	801	60	3450
Avg.	12.0	704	751	45	3400

Particulate Sizing by Aerodynamic Cascade Impactors

Two types of cascade impactors were employed to collect and aerodynamically size fine particulates. The Brink Cascade Impactor (BMS II) was used to sample the inlet of the ESP. The Andersen Sampler (Mark III) was used to sample the outlet of the ESP.

Several runs were conducted using the impactors, and four of these were compiled runs. A compiled run was performed by sampling several constant velocity points and changing the plate (or plates) in the impactor as it became loaded with particulate matter. The compiled runs (No. 6 and 7 Brink and Cmp 1 and 2 Andersen) were conducted to accumulate a sufficient amount of particulate for further analysis.

Brink Cascade Impactor

Seventeen runs using the Brink Cascade Impactor were performed on the ESP inlet to size particles; but due to power losses on the fifth and eighth runs, only fifteen runs produced data. Particles in the inlet flue gas differed greatly in their size distributions depending on whether the inlet grain loading was "high" or "low." Runs 2, 3, 6, 10, and 14 were classified as a group characterized by inlet grain loadings of 1.11 grains/scf or less and identified as having "low" grain loadings. Since runs 1, 4, 7, 9, 11, 12, 13, 15, 16, and 17 had grain loadings of 1.18 grains/scf and higher, they were considered to have "high" inlet grain loadings (Table 15).

Both groups of data were fitted individually and as groups to lognormal and Weibull distributions to determine which distribution better described the particle size distributions observed. The Weibull distribution was a better fit to the individual runs of the low inlet grain loading group; but when the runs were combined and analyzed as a group, the lognormal and Weibull distributions were equally good (Tables 16 and 17). Similar behavior was noted in the high inlet grain loading groups.

The lognormal and Weibull distributions were compared on the basis of the R-square statistic, the error mean square (EMS), the F-value, and a graphical evaluation of the distribution fit to the data. The R-square statistic indicates the fraction of the total variation explained by the fitted distribution. For example, run 1 in Table 16 had the lognormal distribution to explain approximately 85.84 percent of the total variation, while the Weibull distribution fit explained 89.09 percent. The EMS is the residual variation left over after fitting the distribution to the data and is an estimate of the random error in the data. If a fitted distribution is inappropriate for the data, the EMS is inflated. The last column of Table 16 is the ratio of the lognormal EMS to the Weibull EMS. The ratio of 1.2976 for run 1 indicates that using the Weibull distribution reduced the EMS and slightly raised the R-square statistic. For 14 of the 15 runs, the Weibull fits were better than the lognormal fits.

Overall, the Weibull distribution seemed to characterize and describe particle size data better for this set of data. Estimates of the median

TABLE 15. TEST SUMMARY OF BRINK SAMPLING PARAMETERS

Run[1]	Date	Start Time	Duration (min)	Sampling Location	Stack Gas Composition %					Molecular Weight		Stack Temp (°F)	Barometric Pressure (in. Hg)	Static Pressure (in. H_2O)	Brink ΔP (in. Hg)[2]	Sample Volume (acf)[3]	Sample Flow (acfm)[4]	Nozzle Diameter (mm)	Grain Loading (Grain/scf)
					CO_2	O_2	CO	N_2	H_2O	Dry	Wet								
1	8-10-76	12:25	7	Inlet to ESP	11.4	7.4	0	81.2	9.0	30.12	29.03	350	29.70	-8.0	1.8	0.455	0.065	2	1.5591
2	8-10-76	2:48	7	Inlet to ESP	11.4	7.4	0	81.2	9.0	30.12	29.03	350	29.70	-8.0	1.8	0.455	0.065	2	1.1130
3	8-11-76	10:54	7	Inlet to ESP	12.3	6.3	0	81.4	8.4	30.22	29.19	350	29.80	-8.0	1.8	0.455	0.065	2	0.3779
4	8-11-76	1:30	7	Inlet to ESP	11.8	6.2	0	82.0	8.5	30.14	29.10	350	29.80	-8.0	1.8	0.455	0.065	2	1.5575
6 Compiled	8-12-76	12:31 1:22 1:52	5 2.5 2.5	Inlet to ESP	11.4	6.8	0	81.8	8.6	30.10	29.06	350	29.76	-8.0	1.7	0.650	0.065	2	0.7626
7 Compiled	8-13-76	8:10 9:17 10:22 12:15 13:15	5 2.5 2.5 5 5	Inlet to ESP	11.8	7.1	0	81.1	8.4	30.17	29.15	350	29.58	-8.0	1.7	1.300	0.065	2	1.9066
9	8-16-76	9:01	5	Inlet to ESP	11.7	6.1	0	82.2	10.0	30.12	28.90	350	29.61	-8.0	1.7	0.325	0.065	2	1.1867
10	8-16-76	11:00	5	Inlet to ESP	11.7	6.1	0	82.2	10.0	30.12	28.90	370	29.61	-8.0	1.7	0.325	0.065	2	0.4900
11	8-16-76	12:41	5	Inlet to ESP	11.7	6.1	0	82.2	10.0	30.12	28.90	370	29.61	-8.0	1.7	0.325	0.065	2	2.2111
12	8-17-76	8:42	5	Inlet to ESP	11.5	7.4	0	81.1	9.6	30.14	28.97	370	29.68	-8.0	1.7	0.325	0.065	2	1.9202
13	8-17-76	10:07	5	Inlet to ESP	11.5	7.4	0	81.1	9.6	30.14	28.97	370	29.68	-8.0	1.7	0.325	0.065	2	1.8610
14	8-17-76	13:50	5	Inlet to ESP	11.5	7.4	0	81.1	9.6	30.14	28.97	370	29.68	-8.0	1.7	0.325	0.065	2	0.5346
15	8-18-76	10:00	5.5	Inlet to ESP	10.8	7.5	0	81.7	9.2	30.03	28.93	370	29.66	-8.0	1.7	0.358	0.065	2	1.2894
16	8-18-76	12:30	5	Inlet to ESP	10.8	7.5	0	81.7	9.2	30.03	28.93	370	29.66	-8.0	1.7	0.325	0.065	2	2.5630
17	8-18-76	13:05	5	Inlet to ESP	10.8	7.5	0	81.7	9.2	30.03	28.93	370	29.66	-8.0	1.7	0.325	0.065	2	2.9457

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[1] Runs No. 5 and 8 were destroyed in the field due to power loss.
[2] ΔP = pressure difference across the Brinks.
[3] acf = actual cubic feet.
[4] acfm = actual cubic feet per minute.
[5] Grain/scf = grain per standard cubic feet.

TABLE 16. COMPARISON OF THE LOGNORMAL AND WEIBULL DISTRIBUTIONS FITTED TO THE BRINK IMPACTOR DATA FROM COLBERT

	Individual Runs				
	Lognormal		Weibull		Ratio of Lognormal EMS To Weibull EMS
Run No.	R-Square	Error Mean Square (EMS)	R-Square	Error Mean Square (EMS)	
1	0.8584	0.1718	0.8909	0.1324	1.2976
2	0.9072	0.1126	0.9518	0.0586	1.9215
3	0.9457	0.0659	0.9680	0.0388	1.6985
4	0.8456	0.1874	0.8831	0.1419	1.3206
6	0.8617	0.1678	0.9173	0.1004	1.6713
7	0.9036	0.1171	0.9411	0.0714	1.6401
9	0.9642	0.0435	0.9526	0.0576	0.7552
10	0.8978	0.1226	0.9436	0.0677	1.8109
11	0.9406	0.0713	0.9649	0.0421	1.6936
12	0.9203	0.0956	0.9523	0.0573	1.6684
13	0.8779	0.1465	0.9184	0.0980	1.4949
14	0.8945	0.1266	0.9294	0.0848	1.4929
15	0.9116	0.1061	0.9452	0.0658	1.6125
16	0.9461	0.0647	0.9779	0.0266	2.4323
17	0.8706	0.1552	0.8903	0.1316	1.1793

TABLE 17. SUMMARY STATISTICS OF CURVE FITS TO THE BRINK IMPACTOR DATA FROM COLBERT GROUPED RUNS

Inlet Grain Loading	Error Mean Square	R-Square	F-Value	Error Mean Square	R-Square	F-Value
Low[1]	0.1427	0.8346	141.28	0.1425	0.8349	141.61
High[2]	0.2185	0.7373	162.76	0.2204	0.7350	160.84

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[1] Runs 2, 3, 6, 10, and 14.

[2] Runs 1, 4, 7, 9, 11, 12, 13, 15, 16, 17.

particle size for the individual runs and the low and high inlet grain loading groups are summarized in Tables 18 and 19. Figures 5 through 8 show the sample data and the fitted cumulative distributions for both the low and high inlet grain loading data.

The median particle diameter is the particle diameter at which the cumulative mass concentration is 50 percent. Thus, 50 percent of the mass occurs above this diameter and 50 percent occurs below. After fitting a particle size distribution to the data from the impactor, the median particle diameter and a 95-percent confidence interval are estimated.

The median particle size diameters, estimated from the fitted distributions, must be used with caution since the fitted distributions included the cyclone with its accumulated mass loading. Normally, the cyclone is omitted from the analysis; but for this particular set of Brink data, a large fraction of the mass was caught in the cyclone. When the cyclone was omitted from the analysis, the estimate median particle diameter fell outside the range of the sample data. Inclusion of the cyclone data allowed for the estimation, within the range of sample data, of a median particle size for the low inlet grain loading. The high inlet grain loading group still had the median particle diameter fall outside of the sample data range, but the estimate becomes more reasonable.

For the low inlet grain loading group, the lognormal distribution estimate of the median particle size diameter was 4.85 μm, while the Weibull estimate was 4.88 μm. The high inlet grain loading groups which had the lognormal fit gave an estimated median diameter of 12.87 μm and the Weibull fit gave an estimate of 9.20 μm.

Andersen Cascade Impactor

Seven runs using the Andersen Impactor were analyzed from the outlet of the ESP to size particles. A summary of sampling parameters is found in Table 20. The lognormal and Weibull distributions were fitted to the data to determine which distribution best described the particle size distributions observed. The lognormal distribution fit the individual runs and the grouping of the individual runs better than the Weibull distribution (as shown in Table 21). The median particle diameter estimated from the lognormal distribution was 2.77 μm while the Weibull estimate was 3.08 μm. A significant reduction in the mass and size of the particles which entered the ESP due to the variation of the inlet grain loadings was noted. For example, the low grain loading groups from the inlet had 27.39 percent of the particulate less than 2.77 μm as compared to the high grain loading group from the inlet which had only 10.75 percent below 2.77 μm (based on the Weibull fit).

Table 22 summarizes the individual and group estimates of the median particle diameter for both distributions. Figures 9 and 10 show the sample data and fitted cumulative distributions for the Andersen data.

TABLE 18. ESTIMATED MEDIAN PARTICLE DIAMETER IN MICRONS BASED ON INDIVIDUAL RUNS OF BRINK IMPACTOR DATA

Inlet Grain Loading	Lognormal Median Particle Diameter (μm)	Weibull Median Particle Diameter (μm)
Low		
Run 2		
Run 2	5.69	5.91
Run 3	5.62	5.89
Run 6	4.73	5.30
Run 10	4.50	4.92
Run 14	6.02	6.19
High		
Run 1	13.45	11.37
Run 4	13.18	11.05
Run 7	27.16	17.98
Run 9	16.45	11.89
Run 11	26.65	16.74
Run 12	18.12	12.83
Run 13	19.03	14.48
Run 15	18.96	14.26
Run 16	20.20	13.34
Run 17	48.44	26.28

TABLE 19. ESTIMATED MEDIAN PARTICLE DIAMETER IN MICRONS BASED ON GROUPED RUNS OF BRINK IMPACTOR DATA

	Lognormal		Weibull	
Inlet Grain Loading	Median Particle Diameter (μm)	95% Confidence Interval	Median Particle Diameter (μm)	95% Confidence Interval
Low	4.85	3.86-6.09	4.88	3.88-6.13
High	12.87	9.17-18.05	9.20	6.87-12.32

TABLE 20. TEST SUMMARY OF ANDERSEN SAMPLING PARAMETERS

Run	Date	Start Time	Duration (min)	Stack Gas Composition (%)					Molecular Weight		Stack Temp (°F)	Barometric Pressure (in. Hg)	Stack Pressure (in. Hg)	Sample Volume (cf)	Sample Flow Rate (acfm)	Sample Volume (dscf)	Nozzle Diameter (in.)	Grain Loading Grains/scf
				CO_2	O_2	CO	N_2	H_2O	Dry	Wet								
1	8/10/76	14:37	37	11.7	7.2	0.0	81.1	8.7	30.16	29.11	325	29.70	28.90	13.9000	0.58823	13.050	0.25	0.0599
2	8/11/76	09:30	60	12.1	6.4	0.0	81.5	7.7	30.19	29.25	325	29.80	29.00	22.480	0.57880	21.094	0.25	0.0523
3	8/11/76	13:30	70	11.8	6.2	0.0	82.0	9.7	30.14	28.95	325	29.80	29.00	27.000	0.59521	24.793	0.25	0.0610
5	8/12/76	13:35	70	12.4	6.8	0.0	80.8	4.6	30.26	29.69	330	29.76	28.96	27.005	0.55903	24.462	0.25	0.0339
6	8/13/76	07:30	120	11.8	7.1	0.0	81.1	8.4	30.17	29.42	345	29.58	28.78	46.380	0.59342	42.601	0.25	0.0304
7	8/13/76	10:45	120	11.8	7.1	0.0	81.1	6.2	30.17	29.42	345	29.58	28.78	44.920	0.56497	40.558	0.25	0.0313
8	8/16/76	08:05	120	11.7	6.1	0.0	82.2	8.9	30.13	29.06	350	29.61	28.81	45.900	0.61093	42.376	0.25	0.0261
Composite 1	8/16/76	11:30	360	11.7	6.1	0.0	82.2	8.9	30.13	29.06	350	29.61	28.81	140.415	0.60395	131.709	0.25	0.0275
Composite 2	8/17/76	11:40	360	11.5	7.4	0.0	81.1	10.8	30.14	28.83	300	29.68	28.88	133.755	0.57248	125.462	0.25	0.0313

TABLE 21. COMPARISON OF THE LOGNORMAL AND WEIBULL DISTRIBUTIONS FITTED TO THE ANDERSEN IMPACTOR DATA FROM COLBERT

	Lognormal		Weibull		
Run No.	R-Square	Error Mean Square (EMS)	R-Square	Error Mean Square (EMS)	Ratio of Lognormal EMS To Weibull EMS
1	0.9937	0.0082	0.9845	0.0201	0.4080
2	0.9908	0.0119	0.9867	0.0174	0.6839
3	0.9923	0.0101	0.9911	0.0116	0.8707
5	0.9948	0.0068	0.9729	0.0352	0.1932
6	0.9939	0.0080	0.9799	0.0263	0.3042
7	0.9924	0.0099	0.9841	0.0206	0.4806
8	0.9903	0.0126	0.9776	0.0291	0.4330
All Runs Grouped	0.9788	0.0206	0.9661	0.0329	0.6261

TABLE 22. ESTIMATED MEDIAN PARTICLE DIAMETER IN MICRONS BASED ON INDIVIDUAL AND GROUPED RUNS OF ANDERSEN IMPACTOR DATA

Run No.	Lognormal Median Particle Diameter (μm)	Weibull Median Particle Diameter (μm)
1	3.01	3.34
2	2.68	3.01
3	3.23	3.52
5	2.79	3.11
6	2.32	2.62
7	2.50	2.81
8	3.02	3.32
All Runs Grouped	2.77	3.08
95% Confidence Interval	2.67-2.87	2.94-3.23

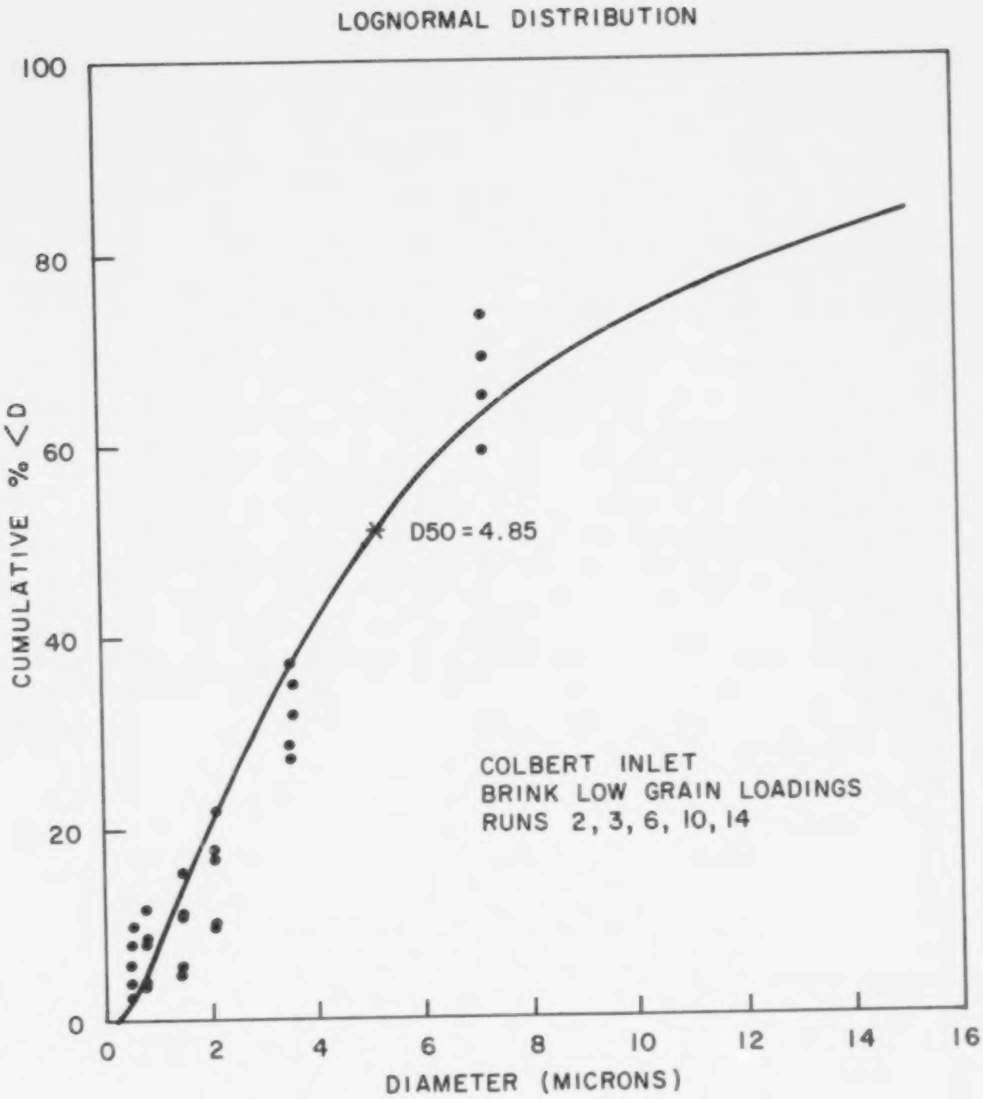

Figure 5. Lognormal distribution plot of runs 2, 3, 6, 10 and 14.

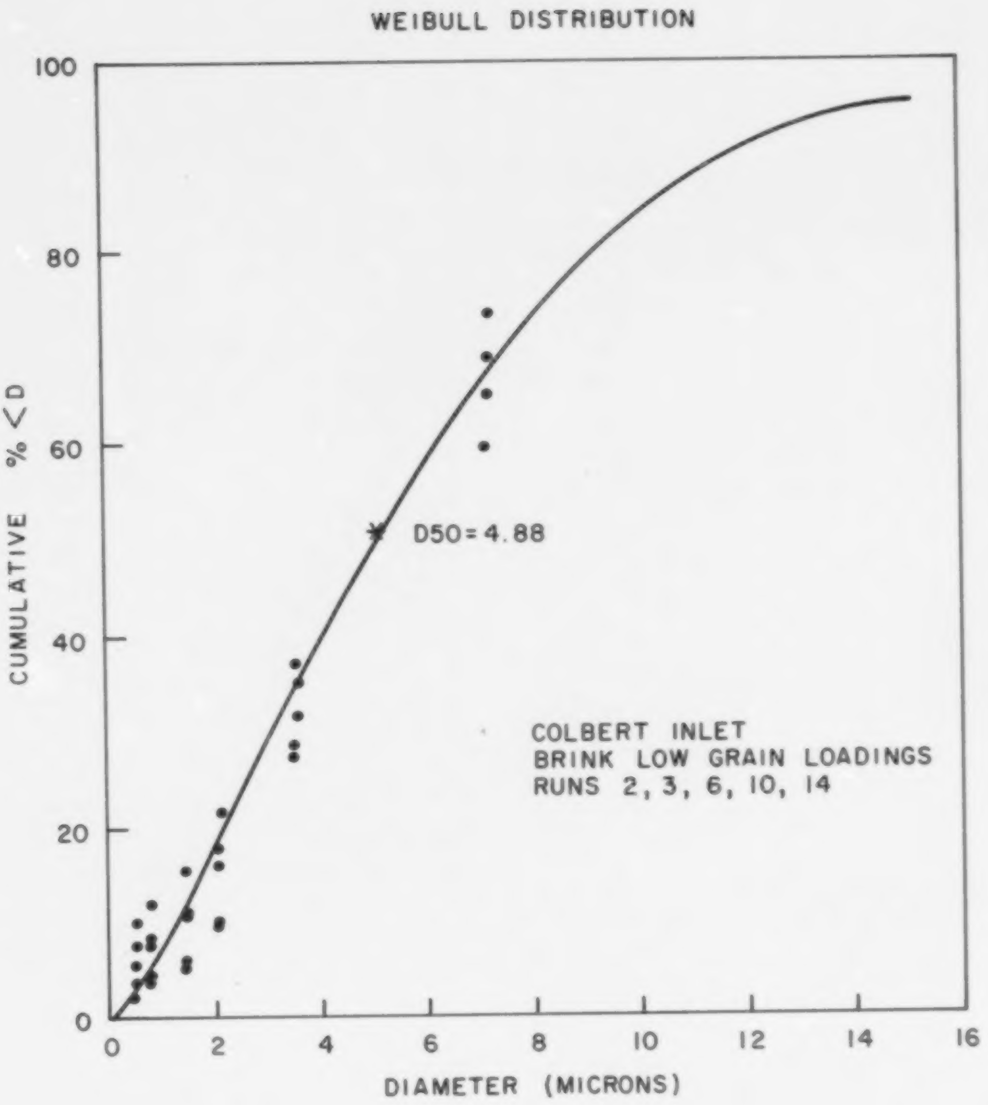

Figure 6. Weibull distribution plot of runs 2, 3, 6, 10 and 14.

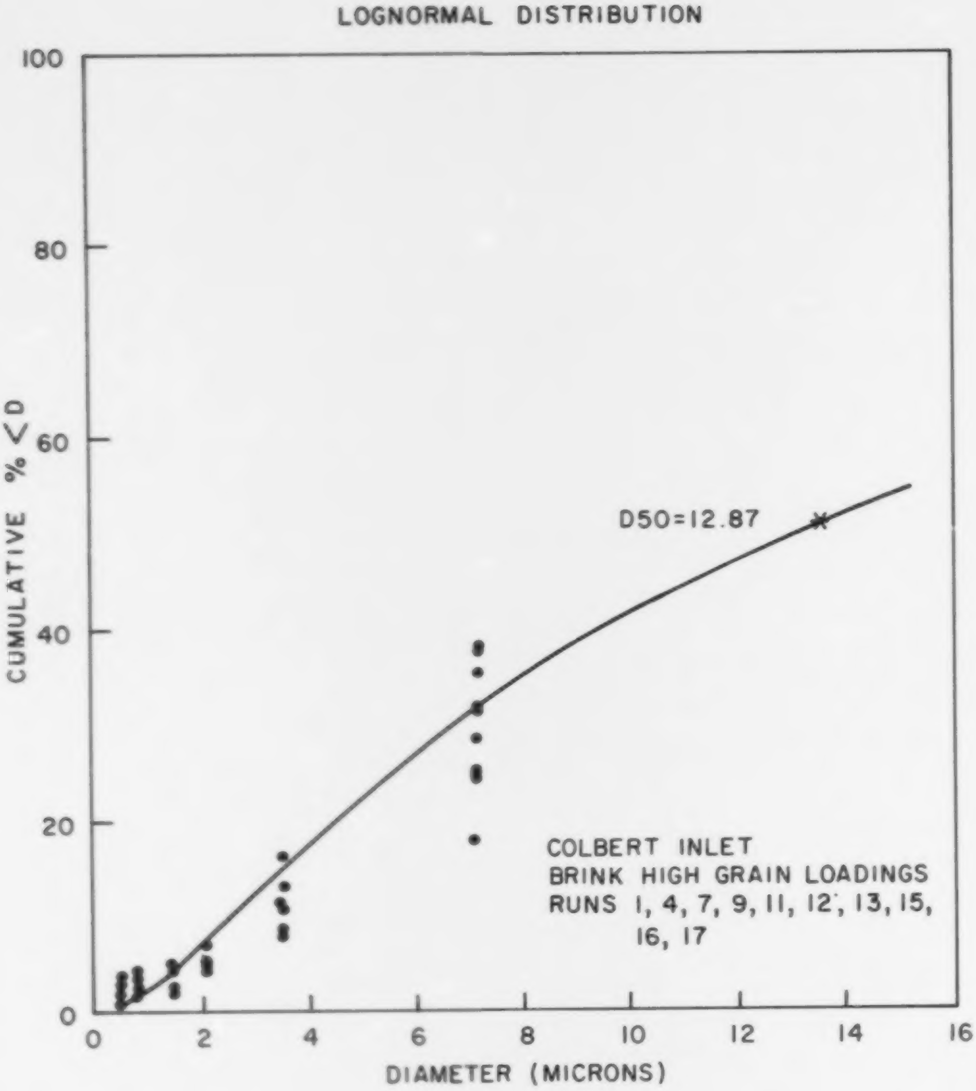

Figure 7. Lognormal distribution of runs 1, 4, 7, 9, 11, 12, 13, 15, 16 and 17.

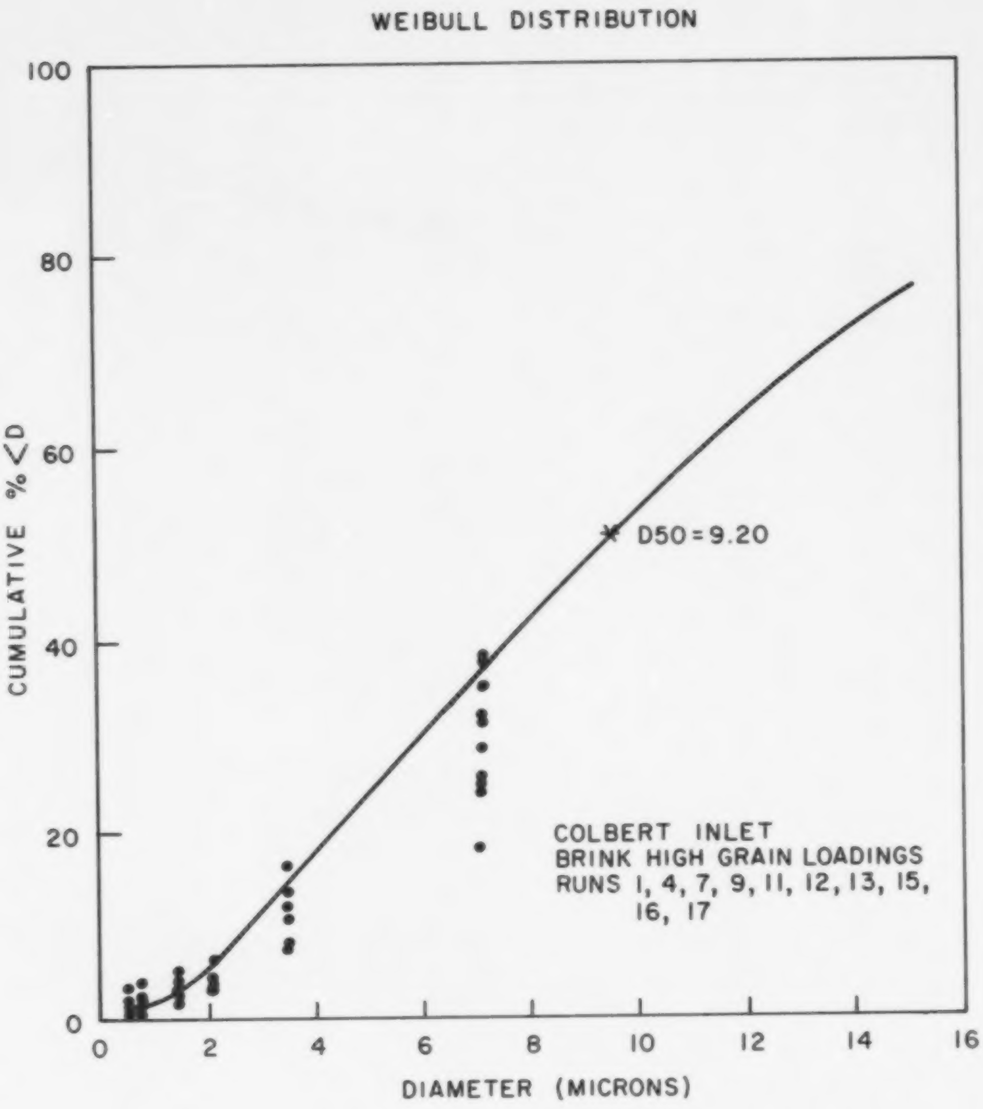

Figure 8. Weibull distribution of runs 1, 4, 7, 9, 11, 12, 13, 15, 16 and 17.

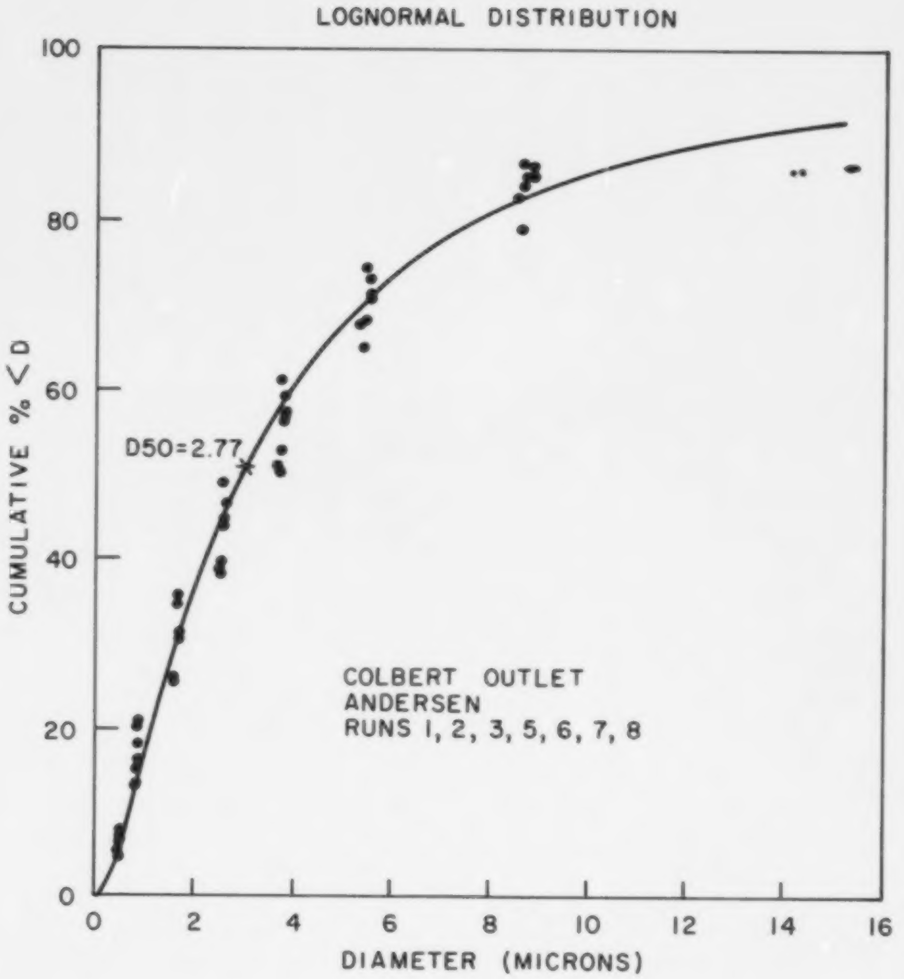

Figure 9. Lognormal distribution plot for Andersen impactor.

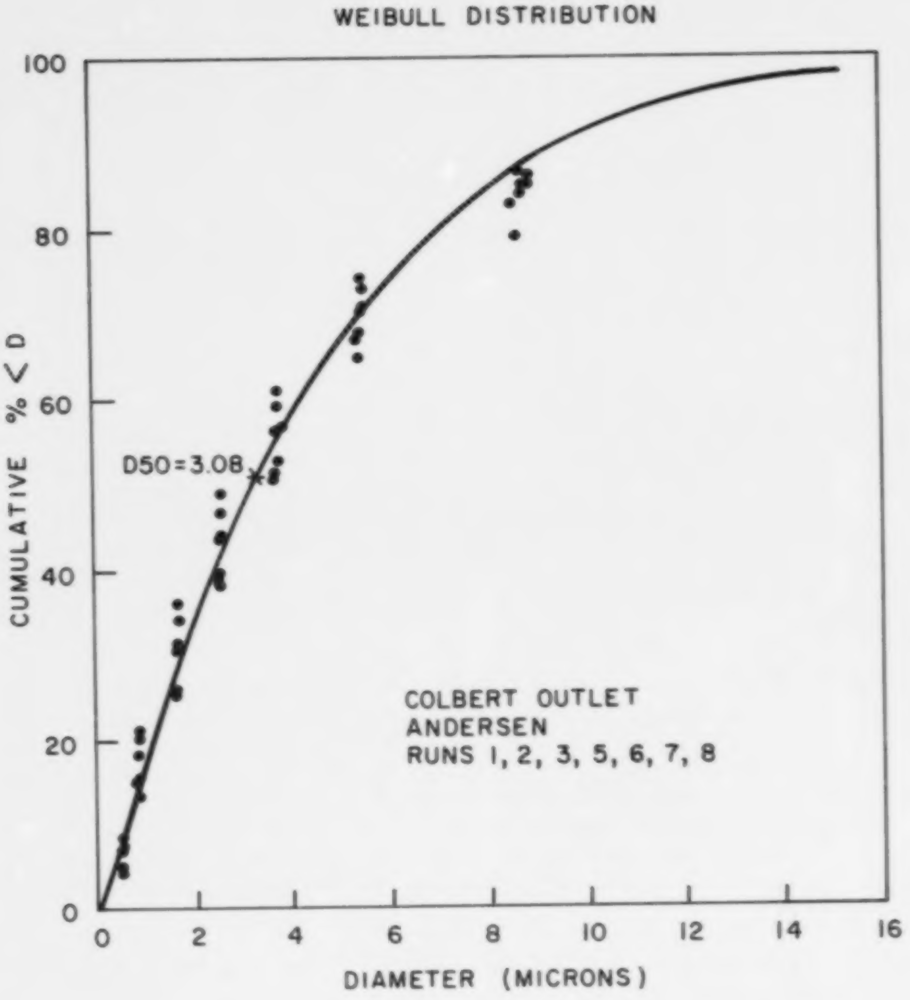

Figure 10. Weibull distribution plot for Andersen impactor.

Size Distribution of Fly Ash by Light Transmission Microscope

Observation of the fly ash particles, as viewed through a light transmission microscope at a low power (10-25x), showed the overall color to be light brown (which was confirmed visually). Approximately 95 percent of the particles appeared spherical in shape, and 80 percent of these spheres had an aspect ratio (ratio of average length to average diameter) of 1.0 to 1.5. The remainder of the particulate sample was composed of black, irregular flakes appearing to be unburned carbon.

Density of Fly Ash by Pycometer

The density of the fly ash sample as determined by a pycometer was found to be 2.263 g/cc.

Particle Counters

The Climet Model 0208A Optical Counter and the General Electric Model 112L428 G1 Condensation Nuclei Counter were used to count the submicron particles. The condensate nuclei counters only count the total number of particles present in a stream; therefore, the Thermo Systems, Inc., Model 3040 Diffusion Battery was used to classify the particle sizes through use of the diffusion principle. Four inlet and four outlet runs were conducted using the Climet Optical Counter, and seven inlet and seven outlet runs were performed using the Diffusion Battery Condensation Nuclei Counter system.

Optical counters are designed to measure low (ambient level) concentrations of particles smaller than 1.5 μm. A dynamic dilution system, designed and built by MRI and consisting of a cyclone with a cutoff diameter of 2.65 μm, was incorporated in front of the counters to dilute and condition the sample continuously. As a result, only particles with diameters smaller than 2.65 μm were allowed to enter the optical instruments. It was found that particles with a diameter of 0.4 μm comprise 80 percent of the total count of particles in the flue gas at both the inlet and outlet.

A graphical stripping technique was used to reduce the collected data. A summary of the inlet data is given in Table 23, and a summary of the outlet data is given in Table 24.

Chemical Characterization of Fine Particulates

Composite samples of a number of runs at both the ESP inlet and outlet were prepared in order to have a sample large enough to chemically analyze. Runs were composited based on the coal analysis; i.e., for the tests in which coal was most similar, the corresponding impactor runs were composited. Table 25 gives a breakdown of the compositing schedule.

Rather than chemically analyzing each stage from the impactors of the various runs conducted, the stages were composited according to particle

TABLE 23. THE CONCENTRATION OF CONDENSATION NUCLEI SIZE PARTICLES (INLET RUNS)

Run No.[1]	% Particle Larger/Smaller than Stated Diameter (μm)	(Corresponding Number of Particle/cm^3) x 10^6 Counter Conditions	Stack Conditions
2	88% > 0.13	19.888	13.647
	9% > 0.085	2.034	1.396
	3% < 0.085	0.678	0.466
3	96% > 0.14	16.032	11.310
	4% > 0.05	0.668	0.471
4	94% > 0.14	17.39	12.043
	6% > 0.088	1.11	0.769
5	92% > 0.14	14.72	10.194
	8% > 0.06	1.28	0.886
6	90% > 0.140	13.41	9.288
	10% > 0.070	1.49	1.032
7	90% > 0.175	13.68	9.562
	10% > 0.070	1.52	1.062
8	95% > 0.130	14.725	10.104
	5% > 0.085	0.775	1.129

---

[1] Run No. 1 was a dry run.

TABLE 24. THE CONCENTRATION OF CONDENSATION NUCLEI SIZE PARTICLES (OUTLET RUNS)

Run No.[1]	% Particle Larger/Smaller than Stated Diameter (μm)	(Corresponding Number of Particle/cm^3) x 10^6	
		Counter Conditions	Stack Conditions
2	14% > 0.200	1.358	0.949
	0.200 > 13% > 0.040	1.261	0.881
	0.040 > 61% > 0.015	5.917	4.136
	0.015 > 9% > 0.010	0.873	0.610
	0.010 > 3%	0.291	0.203
3	9% > 0.050	24.525	17.144
	0.050 > 33% > 0.010	89.925	62.791
	0.010 > 58% > 0.005	158.050	110.482
4	22% > 0.055	20.328	14.468
	0.055 > 6% > 0.040	5.544	3.945
	0.040 > 19% > 0.015	17.556	12.495
	0.015 > 13% > 0.010	12.012	8.549
	0.010 > 40%	36.960	26.306
5	10% > 0.055	35.460	24.784
	0.055 > 7% > 0.025	24.822	17.349
	0.025 > 24% > 0.010	85.104	59.483
	0.010 > 59%	209.214	146.228
6	5% > 0.060	42.030	29.649
	0.060 > 10% > 0.015	84.060	59.297
	0.015 > 85% > 0.005	714.510	504.026
7	8% > 0.060	29.904	20.710
	0.060 > 39% > 0.010	145.782	100.963
	0.010 > 37% > 0.005	138.306	95.785
	0.005 > 16%	59.808	41.421
8	8% > 0.060	28.464	20.078
	0.060 > 13% > 0.015	46.254	32.627
	0.015 > 4% > 0.005	14.232	10.039
	0.005 > 75%	266.850	188.235

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[1] Run No. 1 was a dry run.

TABLE 25. COMPOSITING SCHEDULE FOR CHEMICAL ANALYSIS OF PARTICULATE SAMPLES FROM THE BRINK AND ANDERSEN IMPACTORS

Inlet Duct - Brink Impactor

Test	Runs	Total Sample Weight, g	Stages Composited	Approx. Particle Size, μm
1	(1, 10, 11 15, 16, 17)	0.11766	0c, 1	> 3
		0.02069	2, 3	1-3
		0.00186	4, 5	< 1
1	(2)*	0.01850	0c, 1	> 3
		0.00437	2, 3	1-3
		0.00022	4, 5	< 1
2	(3, 12 13, 14)	0.05146	0c, 1	> 3
		0.00809	2, 3	1-3
		0.00235	4, 5	< 1
2	(4)*	0.02420	0c, 1	> 3
		0.00197	2, 3	1-3
		0.00018	4, 5	< 1
3	(9)	2.18	0c, 1	> 3
		1.91	2, 3	1-3
		1.17	4, 5	< 1
		Outlet Duct - Andersen Impactor		
1	(1, 5)	0.07790	0c, 1, 2, 3	> 3
		0.05327	4, 5	1-3
		0.02963	4, 7, 8	< 1
1	(6)*	0.0327	0c, 1, 2, 3	> 3
		0.02116	4, 5	1-3
		0.03019	6, 7, 8	< 1
2	(2, 3)	0.09556	0c, 1, 2, 3	> 3
		0.07895	4, 5	1-3
		0.03690	6, 7, 8	< 1
3	(7)	0.03601	0c, 1, 2, 3	> 3
		0.01630	4, 5	1-3
		0.03087	6, 7, 8	< 1
4	(8)	0.03509	0c, 1, 2, 3	> 3
		0.01787	4, 5	1-3
		0.01879	6, 7, 8	< 1

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*Analyzed for Cl and F only.

size ranges--<1 μm, 1-3 μm, and >3 μm--for chemical analysis. Tables 26 and 27 give the results of the fine particulate chemical analysis. The analytical results, reported as Test-3 for the inlet and Test-4 for the outlet, were provided by Accu-Lab using Spark Source Mass Spectrometry.

Previous studies[7] indicate that Fe and Al are generally predominate in larger particle sizes; Pb, Sb, Se, Hg, and Zn are concentrated in the smaller particle sizes; and the other elements show either no preference to size or are placed in either category depending on which paper is being reviewed.

After a visual observation of the study results (presented in Tables 25 and 26) it can only be concluded that chemical analysis of such samples are quite difficult and lead to results with a large amount of scatter (orders of magnitude). Error can be introduced at any number of points--sample collection, sample weighing, incomplete recovery of small samples during the preparation for chemical analysis, contamination of samples during physical handling or by the collection substrate, use of two different microchemical analytical techniques, small samples near the limit of sensitivity of the instrument or during the analysis of the blanks.

The large amount of scatter, due to all of the possible sources of error in dealing with extremely small samples, prevents firm conclusions regarding much of the chemical analysis data. There are, however, some trends that might be pointed out for the reader's consideration. The elements in Groups B and C, halogen and volatiles, tended to predominate in the smaller particle size ranges. The elements listed in Group A, except for Ca, tended to predominate in the smaller particle sizes (Brink impactor data only). A majority of the elements in Group D, refractories, showed no trend relating to particle size. Cr, Cu, and Fe tended to concentrate in larger particles and Mn, V, and Zn tended to concentrate in smaller particles (Brink impactor data only).

Emissions Sampling for Organics and Sulfates

During this study GCA/Technology Division, under contract to the U.S. EPA, sampled emissions for organics from the A side of the furnace at the ESP inlet and outlet gas ducts and provided quantitative analysis for sulfate, polychlorinated biphenyls (PCB), and polycyclic organic matter (POM). A traversing gas stream was not employed; instead, a single point representative of the gas stream was sampled. Two samples were obtained at the ESP outlet duct, and one sample was collected at the ESP inlet duct. The results from this study are summarized below.

GCA reports that the ESP grain loading was 3.08 grains/scf, while the average grain loading after the ESP was 0.013 grains/scf. This data indicates a particulate collection efficiency of 99.58 percent for the ESP (A side) on unit 1.

The chemical analysis of the samples taken at the ESP outlet indicated the presence of several organic species, including: alphatic hydrocarbons, aromatic hydrocarbons, carbonyl groups, and alcohols or phenols. The concentration of benzo(a)pyrene in the ESP outlet duct was 0.3 μg/m^3

TABLE 26. CHEMICAL ANALYSIS OF ESP INLET FINE PARTICULATE - BRINK IMPACTOR

Group	Element	Particles >3 µm, µg/g			Particles 1-3 µm, µg/g			Particles <1 µm, µg/g		
		1	2	3*	1	2	3*	1	2	3*
A	Ba	565	718	2150	760	1094	990	2326	1550	1300
	Ca	35502	31706	26700	15400	19800	33830	39200	16300	10735
	Mg	6146	5944	2900	5140	6530	3695	11470	11600	2400
	K	14857	16562	18800	15700	20400	24830	19500	21900	10826
	Na	2996	3314	1700	2930	4045	1110	6580	5400	965
B	Cl	843	1100	280	2425	2740	143	20000	24400	1045
	Fl	324	260	350	617	964	230	<2273	<2778	177
C	Sb	<42	<97	19.4	120	309	33.9	1344	1063	11.6
	As	1275	2914	41.2	3624	9270	20.2	40322	31914	36.0
	Be	9.1	9.8	8.8	10.5	14.0	8.0	16.1	10.6	5.2
	Hg	2.3	0.73	None Detected	0.75	1.67	None Detected	3.23	1.91	None Detected
	Se	2.5	5.8	4.7	<7.3	<18.5	3.8	<80.6	<63.8	7.8
D	Al	74508	75723	33339	58700	78200	59025	74500	77900	39790
	Cd	39.4	12.6	7.9	13.94	86.46	6.6	36.48	11.03	3.2
	Co	<1275	<2914	70.7	3624	9270	38.6	40322	31914	47.1
	Cr	566	616	810	288	247	850	1530	351	282
	Cu	207	118	160	91	110	72.9	285	135	111
	Fe	134586	134460	72000	50400	67300	47124	75700	121200	17140
	Mn	413	416	440	261	376	386	2340	5070	217
	Ni	231	208	140	67	74	318	402	74	65.4
	Si	-	-	84000	-	-	79160	-	-	25740
	Ti	4842	4899	28130	3750	5300	11070	7660	3780	1584
	V	425	517	1710	559	855	1244	1240	660	795
	Zn	847	739	1300	1070	1500	1130	2030	1160	2770
E	Pb	160.1	89.6	88.2	249.0	<93	155	<404	<320	160

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*Accu-Lab Analytical Results

TABLE 27. CHEMICAL ANALYSIS OF ESP OUTET FINE PARTICULATE - ANDERSEN IMPACTOR

Group	Element	Particles >3 µm, µg/g				Particles 1-3 µm, µg/g				Particles <1 µm, µg/g			
		1	2	3	4*	1	2	3	4*	1	2	3	4*
A	Ba	<540	<440	<1168	191.1	<789	<533	<2579	280.4	<1411	<1139	<1362	428
	Ca	24000	24100	26300	22200	28500	28100	21200	63370	25200	21200	23800	31070
	Mg	10200	9310	10600	9455	11800	11600	8700	13100	10300	9100	9740	15147
	K	3890	5940	4800	10386	4970	5940	3750	8151	5900	4380	4950	8720
	Na	17100	11700	31000	46486	20900	14200	54800	65890	37700	31400	37600	53115
B	Cl	11226	-	-	157.4	6857	-	-	252	8980	-	-	133
	Fl	363	-	-	2663	561	-	-	3000	<394	-	-	4679
C	Sb	<32	<26	<69	2.9	<47	<31	<153	1.8	<84	<67	<81	3.1
	As	<963	<784	<2082	4.3	<1407	<949	<4601	1.6	<2531	<2032	<2429	2.6
	Be	0.23	1.92	0.22	<0.34	0.39	1.08	<0.12	0.33	0.71	0.58	0.66	0.84
	Hg	0.34	2.31	2.81	None Detected	0.65	0.25	0.34	None Detected	0.2	2.09	2.98	None Detected
	Se	3.0	8.7	27.5	58.6	2.8	8.2	21.2	17.8	6.7	16.9	21.1	19.7
D	Al	13500	22800	14000	18750	17900	21100	11800	16743	16800	14300	15100	14444
	Cd	3.08	2.63	8.22	<0.80	1.99	3.1	<1.9	1.0	3.60	1.67	1.87	0.97
	Co	<953	<784	<2082	7.19	<1409	<949	<4601	1.48	<2531	<2032	<2429	4.0
	Cr	20.6	75.4	54.5	34.8	26.5	32.8	18.6	18.5	24.6	23.9	26.1	20.7
	Cu	15.0	49.2	20.2	12.9	15.3	17.2	<15	7.09	11.2	9.0	<8	12.9
	Fe	1770	16100	4430	6750	2170	5000	1230	854.8	2600	2570	2680	3550
	Mn	17.7	76.8	37.1	22.9	25.4	39.1	<13.6	12.9	23.7	24.5	30.3	26.5
	Ni	17.5	35.6	24.3	5.32	19.7	20.5	19.7	3.08	26.1	19.7	19.4	8.7
	Si	-	-	-	139510	-	-	-	84000	-	-	-	79645
	Ti	241	950	330.1	272.3	296	547	329.3	176.9	350	414	408.9	747.1
	V	9.2	90.9	13.0	28.2	19.4	55.8	8.3	30.8	47.6	42.7	50.8	121
	Zn	<357	<291	<773	329.5	<523	352	<1709	554.8	<940	<755	<902	412
E	Pb	40.5	32.6	57.0	15.04	24.2	23.6	<22	3.8	24.7	16.4	12.8	19

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*Accu-Lab Analytical Results

(0.4 g/hr), which is about 15 times the MATE Level of 0.02 μg/m^3. Also, the upper limit to PCB emissions (1.7 μg/m^3) was on the order of the background concentration of PCB's over the ocean. Finally, the concentration of sulfate in the flue gas after the ESP was 6.47 mg/m^3 (8,630 g/hr). There is no sulfate MATE value for comparison.

Organic and Other Analyses of Ash Sluice Samples

During this study a number of liquid and dry ash samples were taken for analysis of organic constituents. Monsanto Research Corporation, under contract to EPA, analyzed these samples. Ash slurry samples were filtered and analyzed as both a solid portion and a liquid portion.

Samples were analyzed by GC/MS for polycyclic organic matter (POM) and polychlorinated biphenyls (PCB). No PCB's were detected in any of the samples. POM's were found in all but one of the samples; however, only two samples contained POM's in appreciable quantities (>1 μg) (Table 28).

In addition to organic analysis, the samples were analyzed for total chlorine, ionic chlorine, total organic carbon, and sulfur. The liquid samples were also analyzed with the Jarrell Ash Atomcomp (ICAP) for trace elements. Chlorine concentration ranged in general from 10 to 40 ppm. The elements found in the liquid filtrates at levels in excess of 1 ppm were Ba, B, Ca, Mg, Mo, Na, and S. Tables 28 and 29[8] are taken from the final report. Table 29 also agrees with other data from Table 13.

MASS BALANCE

Determination of Flow Rates

The mass flow rates for the inflow coal and outflow ash streams are presented in Table 30. Coal flow rates for the test periods were based on data from the coal scales and counters; estimates were made for those periods when there was a scale malfunction. The pulverized coal flow rates were determined by subtracting the weight of the measured pyrites and the coal moisture from the weight of the whole coal, provided by the coal scale measurements. The bottom ash flows were determined by subtracting pyrites and the fly ash flows from the total ash of the whole coal flow. The ESP hopper ash flow was derived from the difference between the total particulate trains operated before and after the ESP. All other flows were measured directly. Table 31 contains a summary of all flows for each element.

Material and Flow Analysis - System and Sample Points

The total material flow analysis summed up the individual trace element flows over the eight days of sampling. For the pulverizer, boiler, and ESP, the material flow error was calculated as the sum of the outputs over the total input flow and was expressed as a percentage. For the pulverizer, the material flow error was the sum of all pyrite flows plus all

TABLE 28. POLYCYCLIC ORGANIC MATERIALS - GC/MS[a]

Component	Dry ESP composite, 8/19/76 - μg/g			Colbert pyrite, 8/18/76 - μg/g			Colbert pulverizer, 8/18/76 - μg/g			Dry ESP composite, 8/18/76 - μg/g		
	Fraction			Fraction			Fraction			Fraction		
	2	3	4	2	3	4	2	3	4	2	3	4
Dibenzothiophene	N.D.	N.D.	N.D.	N.D.	0.421	0.521	N.D.	1.422	0.466	N.D.	N.D.	N.D.
Anthracene/phenanthrene	N.D.	N.D.	N.D.	N.D.	9.037	6.502	N.D.	24.932	8.966	N.D.	0.0231	0.0118
Methyl-anthracenes/-phenanthrenes	N.D.	N.D.	N.D.	N.D.	14.545	13.076	N.D.	48.004	16.432	N.D	0.045	N.D.
9 - Methyl-anthracene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dimethyl-anthracenes/-phenanthrenes	N.D.	N.D.	N.D.	N.D.	17.236	14.967	N.D.	53.903	19.315	N.D.	0.0434	N.D.
Fluoranthene	N.D.	N.D.	N.D.	N.D.	0.364	1.223	N.D.	1.012	1.427	N.D.	N.D.	N.D.
Pyrene	N.D.	N.D.	N.D.	N.D.	1.758	1.474	N.D.	4.116	1.612	N.D.	0.0231	N.D.
Methyl-fluoranthenes/-pyrenes	N.D.	N.D.	N.D.	N.D.	4.497	10.236	N.D.	16.349	18.830	N.D.	N.D.	N.D.
Benz(c)phenanthrene	N.D.	N.D.	N.D.	N.D.	0.417	1.351	N.D.	0.611	1.039	N.D.	N.D.	N.D.
Chrysene/benz(a)anthracene	N.D.	N.D.	N.D.	N.D.	1.857	7.298	N.D.	4.132	15.024	N.D.	N.D.	N.D.
7, 12 - Dimethyl-benz(a)anthracenes (or isomers)	N.D.	N.D.	N.D.	N.D.	17.658	18.844	N.D.	20.908	24.485	N.D.	N.D.	N.D.
Benzofluoranthene(s)	N.D.	N.D.	N.D.	N.D.	0.350	1.715	N.D.	1.136	3.713	N.D.	N.D.	N.D.
Benzopyrene(s) (and perylene)	N.D.	N.D.	N.D.	N.D.	0.426	1.502	N.D.	1.553	4.757	N.D.	N.D.	N.D.
3 - Methylcholanthrene	N.D.	N.D.	N.D.	N.D.	N.D.	1.754	N.D.	0.684	1.796	N.D.	N.D.	N.D.
Indeno(1, 2, 3 - cd)pyrene	N.D.	N.D.	N.D.	N.D.	N.D.	1.270	N.D.	N.D.	1.985	N.D.	0.0127	N.D.
Dibenz(a, h)anthracene	N.D.	N.D.	N.D.	N.D.	N.D.	1.038	N.D.	N.D.	2.835	N.D.	N.D.	N.D.
Dibenz(c, g)carbazole	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dibenzopyrenes	N.D.	N.D.	N.D.	N.D.	N.D.	3.436	N.D.	0.606	3.189	N.D.	N.D.	N.D.

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[a] Detection limit for Colbert pyrite and pulverizer is 0.5 μg; for all other samples, limit is 0.025 μg.

N.D. - Not detected.

Table 28. (continued)

Component	ESP fly ash, 8/18/76						ESP fly ash, 8/19/76					
	Liquid phase extract, µg/l			Solids portion, µg/g			Liquid phase extract, µg/l			Solids portion, µg/g		
	Fraction						Fraction					
	2	3	4	2	3	4	2	3	4	2	3	4
Dibenzothiophene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Anthracene/phenanthrene	N.D.	0.056	0.161	N.D.	0.002	N.D.	N.D.	0.845	0.331	N.D.	0.002	N.D.
Methyl-anthracenes/-phenanthrenes	N.D.	0.119	0.305	N.D.	0.002	N.D.	N.D.	1.01	0.553	N.D.	0.005	N.D.
9 - Methyl-anthracene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dimethyl-anthracenes/-phenanthrenes	N.D.	0.161	0.393	N.D.	0.003	N.D.	N.D.	0.804	0.431	N.D.	0.005	N.D.
Fluoranthene	N.D.	0.088	0.084	N.D.	<0.002	N.D.	N.D.	0.092	0.128	N.D.	N.D.	N.D.
Pyrene	N.D.	0.174	0.160	N.D.	<0.002	N.D.	N.D.	0.193	0.160	N.D.	N.D.	N.D.
Methyl-fluoranthenes/-pyrenes	N.D.	N.D.	0.123	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benz(c)phenanthrene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Chrysene/benz(a)anthracene	N.D.	N.D.	0.047	N.D.	N.D.	N.D.	N.D.	0.093	0.047	N.D.	N.D.	N.D.
7, 12 - Dimethyl-benz(a)anthracenes (or isomers)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Benzofluoranthene(s)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.071	N.D.	N.D.	N.D.	N.D.
Benzopyrene(s) (and perylene)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.062	0.035	N.D.	N.D.	N.D.
3 - Methylcholanthrene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.248	N.D.	N.D.	N.D.	N.D.
Indeno(1, 2, 3 - cd)pyrene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dibenz(a, h)anthracene	N.D.	N.D.	0.066	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dibenz(c, g)carbazole	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Dibenzopyrenes	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. - Not detected.

Table 28. (continued)

Component	Bottom ash, 8/18/76						Bottom ash, 8/19/76					
	Liquid phase extract, μg/l			Solids portion, μg/g			Liquid phase extract, μg/l			Solids portion, μg/g		
	Fraction						Fraction					
	2	3	4	2	3	4	2	3	4	2	3	4
Dibenzothiophene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.007	0.04	0.007
Anthracene/phenanthrene	N.D.	0.299	0.064	N.D.	0.010	N.D.	N.D.	0.498	0.430	0.02	0.03	0.041
Methyl-anthracenes/-phenanthrenes	N.D.	0.315	0.125	N.D.	0.017	N.D.	N.D.	0.581	0.466	0.03	0.78	0.068
9 - Methyl-anthracene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<0.003	0.003	<0.003
Dimethyl-anthracenes/-phenanthrenes	N.D.	0.097	0.068	N.D.	0.017	N.D.	N.D.	0.459	0.439	0.01	0.78	0.058
Fluoranthene	N.D.	0.073	N.D.	N.D.	0.003	N.D.	N.D.	0.095	1.29	<0.003	0.03	0.007
Pyrene	N.D.	0.382	0.127	N.D.	0.003	N.D.	N.D.	0.141	1.07	<0.003	0.061	0.010
Methyl-fluoranthenes/-pyrenes	N.D.	0.017	N.D.	N.D.	N.D.	N.D.	N.D.	0.045	0.296	<0.003	0.24	0.047
Benz(c)phenanthrene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.071	<0.003	0.003	<0.003
Chrysene/benz(a)anthracene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.04	<0.003	0.085	0.041
7, 12 - Dimethyl-benz(a)anthracenes (or isomers)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<0.003	0.580	0.021
Benzofluoranthene(s)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<0.003	0.02	0.02
Benzopyrene(s) (and perylene)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	0.270	<0.003	0.02	0.034
3 - Methylcholanthrene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<0.003	0.027	0.014
Indeno(1, 2, 3 - cd)pyrene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<0.003	0.034	0.044
Dibenz(a, h)anthracene	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<0.003	0.03	0.047
Dibenz(c, g)carbazole	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<0.003	<0.003	0.027
Dibenzopyrenes	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. - Not detected.

TABLE 29. TRACE METAL CONCENTRATIONS IN FILTRATE OF ASH SLURRY SAMPLES

Trace metals, Jarrell ash Atomcomp metals (ppm)	Sample - filtrates tested			
	Bottom ash, 8/18/76, 3:27-3:55 p.m.	Bottom ash, 8/19/76	ESP fly ash, 8/18/76, 2:46-3:58 p.m.	ESP fly ash 8/19/76, 12:29-1:20 p.m.
Ag	<0.1	<0.1	<0.1	<0.1
Al	0.1	0.1	<0.1	<0.1
Ba	<0.1	0.1	0.8	1.2
B	<0.1	0.3	5.0	9.4
Ca	28.9	96.1	483.0	555.0
Cd	<0.1	<0.1	<0.1	<0.1
Co	<0.1	<0.1	<0.1	<0.1
Cr	<0.1	<0.1	0.1	0.1
Cu	<0.1	<0.1	<0.1	<0.1
Fe	0.2	<0.1	<0.1	<0.1
Mg	3.1	0.3	<0.1	<0.1
Mn	<0.1	<0.1	<0.1	<0.1
Mo	<0.1	<0.1	1.2	1.8
Na	5.7	6.8	16.7	22.3
Ni	<0.1	<0.1	0.1	0.1
Pb	<0.1	<0.1	<0.1	<0.1
Sb	<0.1	<0.1	<0.1	<0.1
Si	2.9	4.6	1.6	0.7
Sn	<0.1	<0.1	<0.1	<0.1
Sr	0.1	0.1	0.7	0.9
Ti	<0.1	<0.1	<0.1	<0.1
V	<0.1	<0.1	<0.1	<0.1
Zn	<0.1	<0.1	<0.1	<0.1
P	<0.1	<0.1	<0.1	<0.1
Be	<0.1	<0.1	<0.1	<0.1
Zr	<0.1	<0.1	<0.1	<0.1
As	<0.1	<0.1	<0.1	<0.1

TABLE 30. MASS FLOW RATE FOR VARIOUS FLOWS IN SYSTEM

Test	Raw Coal (t/h)	Pulverized Coal Burned (t/h)	Pyrites (t/h)	Bottom Ash (t/h)	ESP Hopper Ash (t/h)	Stack Emission (t/h)	Ash Split Bottom Ash %	Ash Split Fly Ash %
1	64.4	64.2	.20	1.70	7.92	.25	17.2	82.8
2	65.9	65.6	.30	2.19	7.16	.58	22.1	77.9
3	72.1	71.9	.20	2.36	6.81	.38	24.7	75.3
4	66.8	66.6	.20	2.44	6.92	.43	24.9	75.1
5	69.7	69.4	.30	2.54	6.06	1.38	26.2	73.8
6	66.9	66.6	.30	2.14	6.90	.19	23.2	76.8
7	69.9	69.7	.20	3.14	8.26	.16	27.2	72.8
8	66.2	66.0	.20	2.61	8.16	.19	23.8	76.2
Average	67.7	67.5	.24	2.39	7.27	.45	23.7	76.3
σ	2.6	2.6	.05	.42	0.77	.40	3.1	3.1

TABLE 31. SUMMARY OF ELEMENT FLOW RATES (lb/h)

WHOLE COAL (lb/h)

TEST	Al	As	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe	Hg
1	2060	1.93	15.5	0.142	649	0.37	180	0.31	2.24	1.120	6.44	2306	0.041
2	1968	1.70	13.15	0.164	675	0.23	238	0.59	2.35	1.21	7.90	2627	0.040
3	2019	1.15	14.4	0.159	663	0.51	231	0.10	2.12	1.150	8.65	2394	0.036
4	1870	1.34	1.3	0.174	550	0.14	240	0.61	2.65	1.280	1.34	2432	0.036
5	1952	2.37	1.6	0.181	570	0.17	251	0.30	2.66	1.380	13.90	3346	0.031
6	1472	1.47	2.4	0.161	611	0.66	241	0.48	2.46	0.789	10.70	2689	0.031
7	1957	1.26	14.0	0.224	558	0.30	182	0.19	2.88	0.755	22.37	2824	0.032
8	2118	1.19	35.7	0.172	712	0.28	199	0.30	2.50	0.887	26.480	2794	0.037

TEST	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Si	Ti	V	Zn
1	232	94.7	5.28	77.3	1.090	2.29	0.245	0.374	3980	82.2	6.77	4.51
2	275	108.0	6.31	75.2	1.16	2.54	0.269	0.393	3727	96.3	7.94	5.06
3	231	94.5	5.02	72.1	1.05	2.22	0.346	0.389	3648	94.9	8.51	8.54
4	254	104	5.18	86.8	1.08	2.40	0.333	0.454	3621	93.5	10.10	1.51
5	293	105	5.95	105.0	1.56	3.36	0.293	0.390	4210	98.0	10.30	3.76
6	281	103	6.21	87.0	1.61	3.75	0.254	0.388	3372	94.6	9.13	4.78
7	280	111	4.78	83.9	1.22	3.02	0.294	0.419	4166	99.4	13.2	10.4
8	225	132	5.48	86.1	1.46	3.83	0.238	0.450	4488	89.6	8.78	4.34

TABLE 31. (Continued)

PYRITES (lb/h)

TEST	Al	As	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe	Hg
1	7.64	0.048	0.394	0.0	3.71	0.0	0.021	0.020	0.016	0.012	0.022	74	0.0
2	11.30	0.084	0.441	0.001	4.97	0.001	0.006	0.031	0.036	0.025	0.017	144	0.0
3	7.80	0.044	0.186	0.0	2.66	0.0	0.018	0.013	0.015	0.016	0.022	106	0.0
4	7.20	0.044	0.072	0.0	1.87	0.0	0.014	0.015	0.021	0.011	0.015	84	0.0
5	10.50	0.046	0.111	0.001	3.91	0.001	0.027	0.026	0.032	0.022	0.030	151	0.0
6	9.30	0.043	0.363	0.001	5.02	0.001	0.037	0.021	0.034	0.019	0.030	129	0.0
7	7.64	0.022	0.108	0.0	3.70	0.0	0.027	0.018	0.017	0.011	0.022	92	0.0
8	11.80	0.028	0.080	0.0	3.48	0.0	0.014	0.018	0.022	0.013	0.032	82	0.0

TEST	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Si	Ti	V	Zn
1	1.58	0.560	0.054	0.186	0.011	0.041	0.001	0.003	12.0	0.294	0.027	0.112
2	3.32	1.090	0.085	0.274	0.050	0.100	0.002	0.004	20.8	0.642	0.086	0.153
3	1.70	0.600	0.048	0.110	0.028	0.089	0.001	0.003	12.2	0.343	0.029	0.057
4	1.34	0.436	0.038	0.130	0.020	0.052	0.001	0.004	12.4	0.274	0.031	0.034
5	2.38	0.882	0.093	0.195	0.056	0.119	0.001	0.006	18.9	0.481	0.045	0.061
6	3.05	1.040	0.238	0.186	0.034	0.106	0.002	0.005	16.5	0.630	0.068	0.116
7	2.10	0.740	0.073	0.226	0.018	0.065	0.001	0.008	16.3	0.390	0.035	0.107
8	2.24	0.692	0.061	0.343	0.025	0.062	0.001	0.007	26.3	0.398	0.026	0.050

TABLE 31. (Continued)

PULVERIZED COAL (lb/h)

TEST	Al	As	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe	Hg
1	2208	1.54	23.10	0.180	542	0.130	231	3.210	3.30	2.39	5.260	2889	0.019
2	1967	2.10	12.50	0.133	442	0.040	249	4.720	3.07	1.64	1.320	3016	0.013
3	2114	3.45	7.80	0.187	413	0.140	230	0.431	3.11	1.58	5.180	2962	0.014
4	1931	2.26	9.30	0.153	352	0.040	266	2.400	2.73	1.44	0.666	2811	0.013
5	1943	2.64	11.80	0.162	401	0.050	278	2.500	3.12	1.61	6.380	3331	0.017
6	1931	2.13	13.30	0.125	374	0.120	240	1.330	2.17	1.35	2.130	3610	0.016
7	2091	2.65	5.60	0.222	580	0.130	223	2.370	4.13	1.81	3.070	3346	0.014
8	2006	2.77	9.10	0.189	533	0.060	211	1.980	3.21	1.69	5.280	2970	0.017

TEST	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Si	Ti	V	Zn
1	453	121.0	7.07	53.5	2.311	2.311	0.26	0.514	4404	93.9	9.78	6.93
2	394	98.3	6.18	49.2	2.229	2.491	0.27	0.616	3540	84.0	9.06	5.91
3	380	97.2	5.42	45.9	2.013	2.013	0.27	0.532	3451	85.6	9.79	5.54
4	388	94.3	5.10	49.7	1.998	2.131	0.37	0.626	3037	83.9	9.26	5.47
5	390	91.7	6.55	59.0	2.360	2.637	0.33	0.611	4442	83.4	10.50	6.30
6	328	82.6	5.51	36.6	1.998	2.664	0.31	0.599	3397	65.3	7.62	5.21
7	502	148.0	6.94	38.3	1.952	2.370	0.35	0.767	3694	102.0	10.60	7.58
8	498	139.0	6.10	42.1	1.980	5.676	0.29	0.409	3036	94.9	10.30	4.86

TABLE 31. (Continued)

BOTTOM ASH (lb/h)

TEST	Al	As	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe	Hg
1	323	0.014	3.18	0.027	105.0	0.001	0.06	0.136	0.557	0.249	0.017	646	0.0
2	430	0.022	5.00	0.031	115.0	0.003	0.23	0.215	0.667	0.296	0.022	855	0.0
3	425	0.038	3.37	0.030	93.9	0.0	0.12	0.165	0.666	0.275	0.024	944	0.0
4	374	0.073	3.80	0.034	155.0	0.004	0.17	0.249	0.677	0.341	0.024	892	0.0
5	416	0.061	3.61	0.034	114.0	0.003	0.20	0.208	0.782	0.350	0.010	976	0.0
6	357	0.030	4.50	0.026	86.6	0.0	0.07	0.223	0.884	0.276	0.0	974	0.0
7	534	0.050	5.37	0.023	92.4	0.004	0.180	0.245	0.754	0.241	0.031	1225	0.001
8	463	0.042	2.87	0.028	97.7	0.002	0.14	0.235	0.601	0.288	0.0	898	0.0

TEST	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Si	Ti	V	Zn
1	72.0	22.70	2.03	8.9	0.340	0.323	0.014	0.002	540	23.7	1.57	0.877
2	79.8	24.50	1.54	11.9	0.439	0.403	0.014	0.002	597	17.6	1.88	0.934
3	74.1	19.10	1.20	12.2	0.444	0.335	0.020	0.004	632	17.0	1.78	0.651
4	80.4	27.50	1.52	11.8	0.487	0.541	0.024	0.005	775	18.8	2.09	1.140
5	84.9	25.40	1.90	14.0	0.559	0.513	0.023	0.004	767	20.4	2.22	1.140
6	69.5	20.30	1.47	10.6	0.399	0.399	0.016	0.003	566	15.2	1.82	0.759
7	74.8	21.40	1.14	18.3	0.628	0.528	0.033	0.003	955	14.1	1.34	0.672
8	96.6	22.80	1.17	15.3	0.595	0.423	0.016	0.003	742	19.0	1.65	0.637

TABLE 31. (Continued)

ESP INLET (lb/h)

TEST	Al	As	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe	Hg
1	1635	1.36	21.30	0.145	497	0.245	113.0	0.719	9.27	1.33	6.87	1814	0.452
2	1548	1.39	15.60	0.157	413	0.209	70.7	0.691	11.40	1.54	6.19	1808	0.226
3	1438	1.42	10.20	0.150	328	0.187	40.3	0.589	6.83	1.32	3.74	1624	0.040
4	1469	1.20	11.90	0.138	339	0.250	41.1	0.676	5.38	1.30	3.60	1586	0.026
5	1442	1.49	14.60	0.159	394	0.193	75.8	0.699	7.54	1.47	4.61	1680	0.050
6	1419	1.42	13.90	0.152	351	0.184	41.2	0.596	7.31	1.30	3.48	1533	0.030
7	1684	1.33	9.94	0.173	318	0.185	42.1	0.775	10.20	1.40	3.87	1652	0.020
8	1671	1.35	9.10	0.174	403	0.234	63.5	0.769	12.10	1.440	5.01	1526	0.017

TEST	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Si	Ti	V	Zn
1	263	97.6	7.65	75.2	2.24	1.380	0.294	0.311	3073	87.3	7.80	9.460
2	275	88.6	6.41	69.7	3.03	1.210	0.381	0.223	2950	85.0	8.47	9.780
3	292	74.0	4.93	66.1	2.93	0.881	0.244	0.244	2746	75.9	8.01	8.110
4	153	75.9	4.99	64.6	2.03	1.460	0.176	0.294	2805	72.7	7.73	9.300
5	329	88.5	6.99	71.4	2.50	1.680	0.282	0.282	2854	84.0	8.55	10.900
6	281	80.5	5.97	69.5	2.37	1.370	0.440	0.270	2725	74.4	8.69	9.450
7	300	81.0	4.65	70.7	3.18	0.756	0.253	0.253	3285	89.3	8.14	7.560
8	394	97.6	5.23	75.2	3.69	0.602	0.318	0.318	3409	93.3	8.76	9.110

TABLE 31. (Continued)

ESP HOPPER (lb/h)

TEST	Al	As	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe	Hg
1	1442	0.396	17.40	0.181	646	0.143	1.59	0.380	2.41	1.250	1.110	2393	0.003
2	1384	0.453	14.90	0.130	584	0.064	2.87	0.397	2.06	1.090	1.060	2115	0.010
3	1307	0.177	9.12	0.128	456	0.004	0.05	0.449	1.89	1.010	1.360	2042	0.001
4	1369	1.080	9.13	0.119	492	0.004	1.25	0.484	1.87	0.985	0.968	2144	0.001
5	1212	0.400	12.10	0.114	395	0.073	1.15	0.727	1.72	0.889	0.121	1854	0.011
6	1298	0.469	13.50	0.130	489	0.002	0.83	0.594	2.76	0.941	0.966	2057	0.007
7	1587	2.980	13.70	0.113	516	0.182	0.04	0.925	1.55	0.767	0.826	1801	0.002
8	1567	1.050	11.80	0.173	617	0.002	1.18	1.010	2.30	1.200	0.327	2433	0.014

TEST	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Si	Ti	V	Zn
1	271	111.0	6.720	60.2	1.340	1.190	0.151	0.063	3185	94.9	8.58	8.81
2	250	91.3	6.040	53.7	1.180	1.170	0.187	0.055	2735	80.6	7.07	7.35
3	244	79.2	4.760	54.5	1.080	0.950	0.204	0.082	2573	73.9	6.66	5.83
4	253	85.6	5.140	58.1	1.050	0.863	0.249	0.046	2697	75.8	6.65	6.13
5	231	72.3	4.650	47.2	1.020	0.912	0.121	0.048	2375	66.9	7.03	5.79
6	208	77.9	5.980	60.7	0.988	1.030	0.207	0.069	2775	68.3	7.33	6.99
7	203	92.5	5.420	67.8	0.878	1.100	0.231	0.078	3223	49.9	5.42	6.30
8	297	115.0	5.580	66.9	1.280	1.330	0.261	0.103	3249	103.0	8.52	7.41

TABLE 31. (Continued)

ESP OUTLET (lb/h)

TEST	Al	As	Ba	Be	Ca	Cd	Cl	Co	Cr	Cu	F	Fe	Hg
1	6.81	0.091	0.084	0.001	3.88	0.026	1.36	0.415	14.10	0.135	0.011	95.2	0.003
2	5.37	0.24	0.060	0.002	3.23	0.046	4.13	1.260	45.00	0.259	0.075	251.0	0.012
3	5.64	0.183	0.064	0.001	4.51	0.066	22.50	0.374	17.10	0.490	0.032	70.1	0.016
4	3.79	0.101	0.034	0.001	2.47	0.035	12.10	1.030	27.10	0.257	0.117	180.0	0.002
5	3.94	0.292	0.058	0.003	7.18	0.084	9.19	2.750	130.00	1.070	0.311	550.0	0.010
6	3.95	0.369	0.031	0.001	2.41	0.038	1.37	0.235	15.20	0.464	0.062	38.7	0.004
7	3.56	0.121	0.006	0.001	2.07	0.018	11.50	0.142	11.30	0.509	0.003	24.5	0.015
8	4.83	0.312	0.034	0.001	2.39	0.017	0.62	0.159	4.98	0.191	0.040	29.7	0.011

TEST	K	Mg	Mn	Na	Ni	Pb	Sb	Se	Si	Ti	V	Zn
1	1.38	1.050	1.800	0.0	4.28	0.020	0.030	0.001	0.0	0.315	0.086	0.238
2	2.89	0.895	5.800	0.0	11.10	0.049	0.122	0.002	0.0	0.263	0.140	0.690
3	1.21	0.914	1.870	0.0	7.36	0.056	0.050	0.001	0.0	0.203	0.092	0.595
4	1.02	0.687	4.570	0.0	11.50	0.048	0.077	0.003	0.0	0.125	0.107	0.592
5	2.69	0.969	14.900	0.0	58.10	0.103	0.315	0.016	0.0	0.181	0.338	2.640
6	1.98	0.627	0.805	0.0	6.90	0.037	0.046	0.001	0.0	0.182	0.081	0.596
7	1.11	0.388	0.518	0.0	6.14	0.027	0.032	0.007	0.0	0.163	0.065	0.305
8	1.52	0.591	0.432	0.0	2.39	0.023	0.016	0.009	0.0	0.239	0.059	0.313

pulverized coal flows divided by the total whole coal flows. The resulting error around the pulverizer was +3.7 percent. Similarly, the boiler material flow error was the total bottom ash flows plus the ESP inlet flows divided by the total pulverized coal flow. The error around the boiler was -6.8 percent. Estimating the error around the ESP as the sum of the outlet and hopper flows divided by the total inlet flow yielded a +5.8 percent error. Table 32 summarizes the material flows and the estimates of the material flow errors.

The material flows were also analyzed to identify significant shifts in flow from test-to-test. Table 33 shows the material flows by test for whole coal, pyrites, pulverized coal, bottom ash, and the inlet, hopper, and outlet of the ESP. Tests 1 and 8, upon closer examination of the data, revealed large differences between whole coal and pulverized coal flows, and between the ESP inlet and ESP hopper. The material flows compared here should match closely (within a couple of hundred lb/h on the average) when the system is operating. Since the flows matched well for the other tests, a possible error occurred on tests 1 and 8. Further investigation did not identify the source of error, but these tests were noted as possibly being in error.

Material flows around the pulverizer, boiler, and ESP were calculated on a daily basis in order to identify tests that may have been impacted by a malfunction. The error percentages are summarized in Table 34. Again, tests 1 and 8 stand out as either having large errors compared to the other tests or having an error in the opposite direction from the other tests. For example, the largest error on the pulverizer occurred on test 1; and although most of the errors are positive, an extremely large negative error occurred on test 8. The loop around the boiler had consistently negative errors (the largest occurring on test 1) while the only positive error occurred on test 8. The loop around the ESP did not show the same pattern of errors in the material balance. Tests 2 and 7 showed extremely good and consistent material balances throughout the system.

Examination of the whole coal and pulverized coal daily averages and standard deviations showed expected behavior. The pyrites do not constitute a significant proportion removed from the whole coal material flow. The standard deviations for the whole coal and pulverized coal are not significantly different.

The standard deviation of the daily pyrite flows relative to the mean indicated substantial variation in the daily pyrite flows. Sometimes this is an indicator of an erroneous or atypical value inflating the estimate of the variance. Examination of daily pyrite flows in Table 33 indicated two flows around 100 lb/h, three flows near 130 lb/h, and two flows near 190 lb/h. Thus, the relatively large standard deviation was not due to one extremely high or low daily material flow.

The other flows which stood out as having relatively large standard deviations were the bottom ash and ESP outlet flows. For the daily bottom ash flows, two values stood out as being relatively different--test 1 had a low flow and test 7 had a high flow. These were noted for further

TABLE 32. TOTAL MATERIAL FLOWS OF TRACE ELEMENTS AND ESTIMATED ERRORS AROUND THE PULVERIZER, BOILER, AND ELECTROSTATIC PRECIPITATOR

Σ of Tests 1 through 8

Sample Point	Total Flow (lb/h)	Loop	Error %
Whole Coal	79,579.93		
Pyrites	1,134.36	Pulverizer	+3.7
Pulverized Coal	81,385.05		
Bottom Ash	18,314.00	Boiler	-6.8
ESP Inlet	57,569.63		
ESP Hopper	59,107.50	ESP	+5.8
ESP Outlet	1,813.75		

TABLE 33. TOTAL MATERIAL FLOWS OF TRACE ELEMENTS BY TEST (ROUNDED TO NEAREST lb/h)

Sample Point	Test							
	1	2	3	4	5	6	7	8
Whole Coal	9,710	9,840	9,502	9,281	10,978	8,996	10,337	10,936
Pyrites	101	188	132	108	189	166	124	128
Pulverized Coal	11,064	9,892	9,826	9,057	11,077	10,112	10,775	9,584
Bottom Ash	1,751	2,143	2,226	2,346	2,429	2,110	2,946	2,363
ESP Inlet	7,726	7,375	6,734	6,657	7,081	6,632	7,575	7,791
ESP Hopper	8,255	7,340	6,863	7,211	6,290	7,077	7,581	8,491
ESP Outlet	131	333	133	246	785	74	63	49

TABLE 34. ESTIMATED ERRORS AROUND THE PULVERIZER, BOILER, AND ELECTROSTATIC PRECIPITATOR BY TEST

Test	Pulverizer	Boiler	ESP
1	+15.0%	-14.3%	+ 8.5
2	+ 2.4%	- 3.8%	+ 4.0
3	+ 4.8%	- 8.8%	+ 3.9
4	- 1.3%	- 0.6%	+12.0
5	+ 2.6%	-14.1%	- 0.1
6	+14.3%	-13.5%	+ 7.8
7	+ 5.4%	- 2.4%	+ 0.9
8	-11.2%	+ 6.0%	+ 9.6
Total	+ 3.7%	- 6.8%	+ 5.8%

investigation, but no explanation was found for these values. The ESP outlet figures showed extremely large variation consistently throughout the daily flows. Again, further investigation did not reveal any apparent errors or explanation for the large variation.

The average daily flow and the standard deviation of the daily flows by sample point were examined to determine which sample points experienced the largest day-to-day variation. Table 35 summarizes the comparison of all 8 tests and tests 2-7. The daily flows for the ESP outlet show an extremely large variation in both cases. Using tests 2-7 reduced the variance of pulverized coal about 3 percent, bottom ash 17 percent, ESP inlet 32 percent, ESP hopper 61 percent, and increased the variance at the ESP outlet by 22 percent. The table indicates that there was no significant difference in the average daily flows of the whole coal and pulverized coal. After removing tests 1 and 8 from the data for the ESP, the inlet and hopper data behaved as expected; but there was still significant variation in the outlet data. The amount of variation in all eight test flows, when compared to the magnitude of the average test flows, indicated that the sample points having the largest variability were the ESP outlet, the pyrites, and the bottom ash. The remaining sample points had a standard deviation less than 10 percent of the mean. When looking at tests 2-7, the results were the same; relative to the size of the average daily flow, the largest test-to-test variability occurred at the ESP outlet, the pyrites, and the bottom ash. The source of the variability does not appear to be the variability of the whole coal put into the system alone. One source of variation might have been operating variability in the pulverizer and boiler. The operating variability of the ESP depends on many factors (such as control settings); but after day 5, the large change at the ESP outlet for small changes at the inlet strongly suggest that the collection efficiency was improved through some maintenance operation. Other possibilities for the variability were the use of an inappropriate sampling technique or a change in the coal.

Material Flow Analysis - By Trace Element

The total material flows over all eight tests for each of the 25 trace elements in the whole coal, the percentage of the total whole coal flow, and identification of large and small flows are presented in Table 36. The five elements with the largest flows and the six elements with the smallest flows are shown in Figure 11. The sum of five elements accounted for 94.4 percent of the total 79,580 lb/h of trace elements in the whole coal. Figure 11 also shows which six elements had extremely small flows. These estimates must be viewed cautiously since they border on the limits of instrument detectability, and/or since they may be subject to large errors in the flow rate. Difficulty in estimating flow rates is detailed elsewhere in this report.

Material flows around the pulverizer, boiler, and ESP were calculated for each trace element for the eight days of testing combined. Figures 12, 13, and 14 present the results; and Table 37 summarizes those elements with flows of 100 lb/h or more as those elements account for 99.4 percent of the total flow. Examination of Figures 12, 13, and 14 allowed identification of elements which had errors in excess of ±10

TABLE 35. MEAN AND STANDARD DEVIATION OF DAILY FLOWS OF TRACE ELEMENTS (in lbs/h) BY SAMPLE POINT

Point	All 8 Tests Mean	All 8 Tests Standard Deviation	Test 2-7 Mean	Test 2-7 Standard Deviation
Whole Coal	9,947.5	737.42	9,822.4	732.04
Pyrites	141.8	34.52	151.0	34.50
Pulverized Coal	10,173.2	733.70	10,122.9	722.88
Bottom Ash	2,289.3	339.65	2,366.7	308.56
ESP Inlet	7,196.2	484.96	7,008.8	400.30
ESP Hopper	7,388.4	718.80	7,060.2	447.98
ESP Outlet	226.7	245.85	272.3	272.01

TABLE 36. SUMMATION OF MATERIAL FLOWS (lb/h) FOR TRACE ELEMENTS IN WHOLE COAL

Element	Total Flow	% of Whole Coal Flow	Five Largest Flows Ranked	Six Smallest Flows Ranked
Al	15,416.0	19.37	3	
As	12.4	0.02		
Ba	98.0	0.12		
Be	1.4	0.00		2
Ca	4,988.0	6.27	4	
Cd	2.7	0.00		4
Cl	1,762.0	2.21		
Co	2.9	0.00		5
Cr	19.9	0.03		
Cu	8.6	0.01		
F	97.8	0.12		
Fe	21,412.0	26.91	2	
Hg	0.3	0.00		1
K	2,071.0	2.60	5	
Mg	852.2	1.07		
Mn	44.2	0.06		
Na	673.4	0.85		
Ni	10.2	0.01		
Pb	23.4	0.03		
Sb	2.3	0.00		3
Se	3.3	0.00		6
Si	31,212.0	39.22	1	
Ti	748.5	0.94		
V	74.7	0.09		
Zn	42.9	0.05		

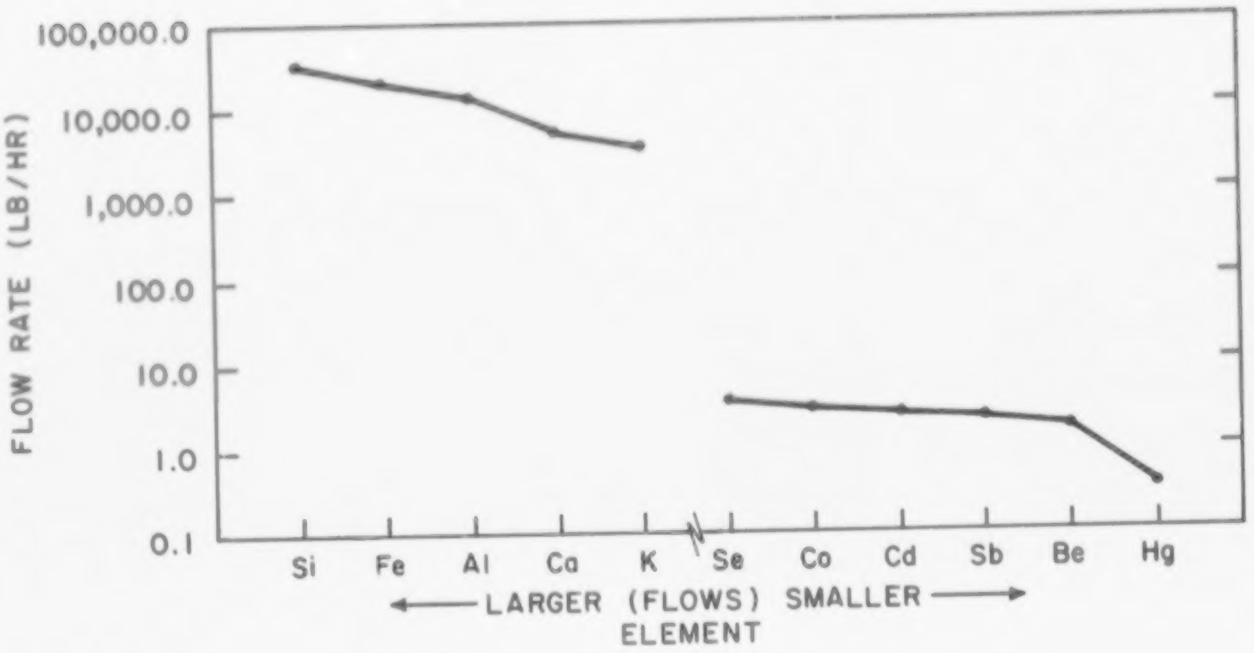

Figure 11. Largest and smallest total flows.

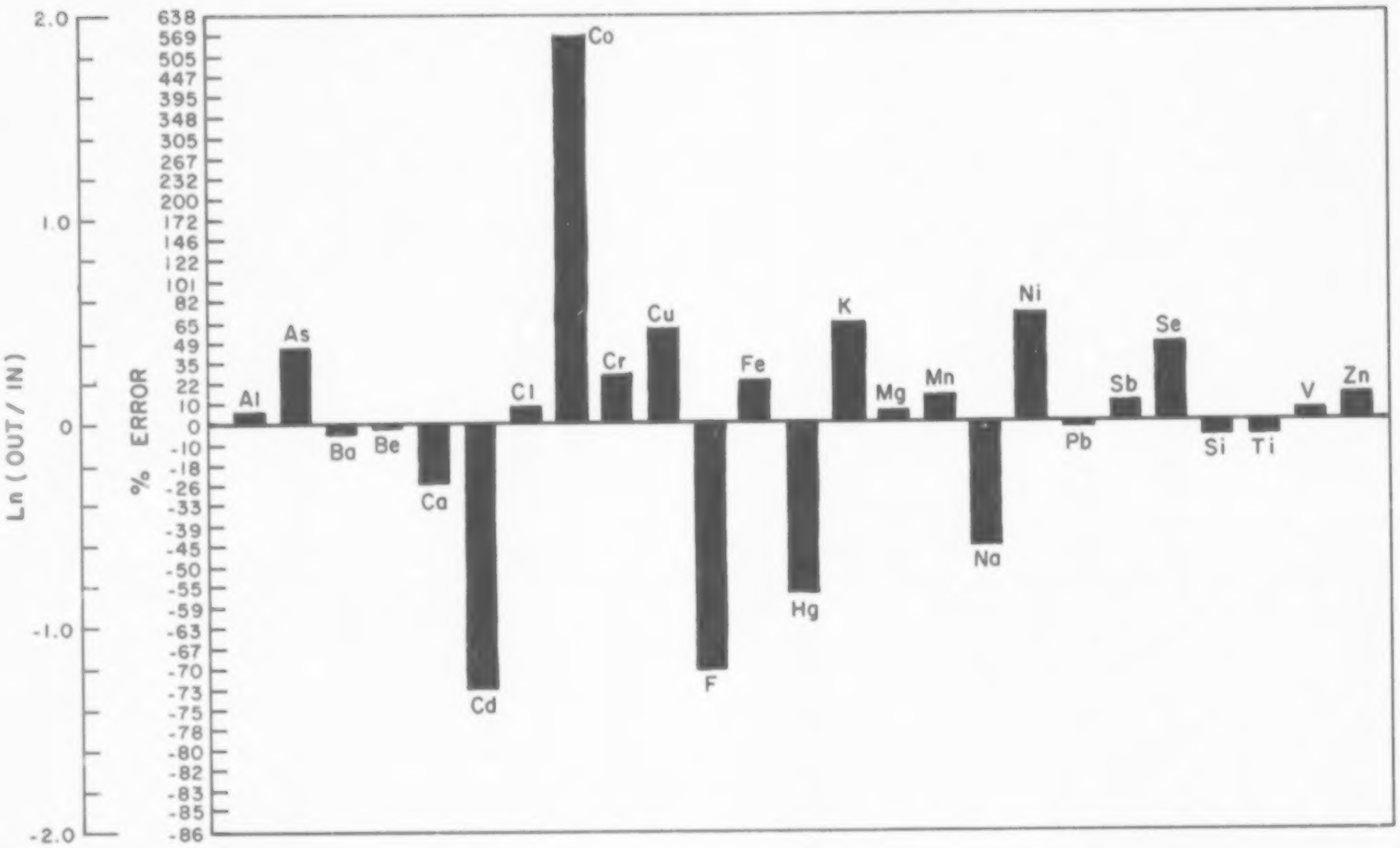

Figure 12. Errors in the material balance by trace element around the pulverizer.

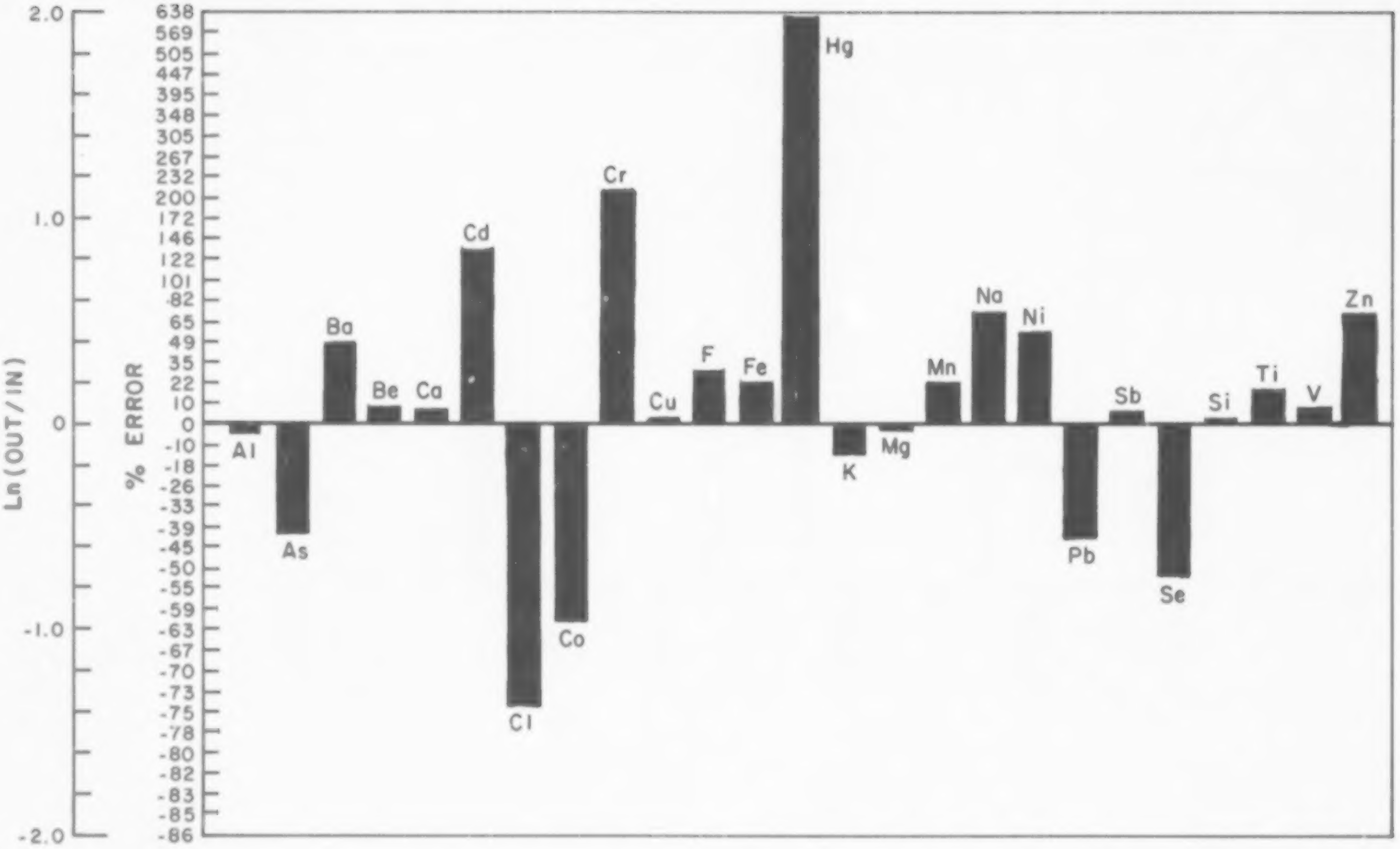

Figure 13. Errors in the material balance by trace element around the boiler.

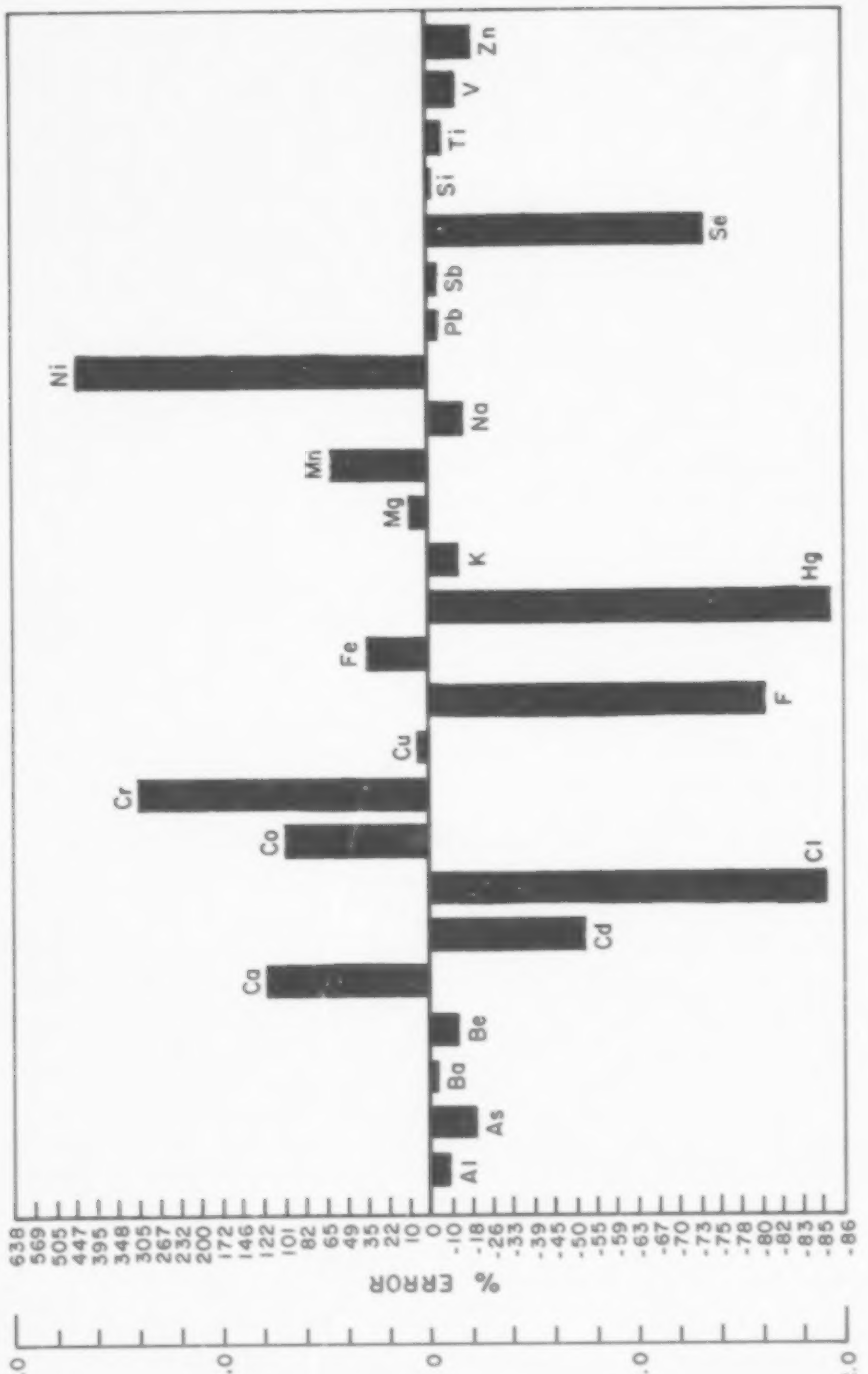

Figure 14. Errors in the material balance by trace element around the ESP.

TABLE 37. ERRORS IN MATERIAL BALANCES FOR TRACE ELEMENTS WITH LARGE TOTAL FLOWS[1]

Element	Total Flow	% Pulverizer Error	% Boiler Error	% ESP Error
Si	31,212.0	-6.6	+1.4	-4.4
Fe***	21,412.0	+20.5	-17.3	+36.7
Al	15,416.0	+5.5	-3.5	-9.0
Ca***	4,988.0	-26.5	+7.3	+38.8
K***	2,071.0	+61.8	-12.4	-13.8
Mg	852.2	+3.0	-0.5	+6.9
Ti	748.5	-7.0	+16.6	-7.1
Na***	673.4	-44.2	+77.8	-16.6

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[1] Summed over the eight days.

***Errors in excess of ±10% in at least two loops.

percent for two or more of the loops around the pulverizer, boiler, or ESP. The troublesome elements are identified by three asterisks. Because only 14 of the 25 trace elements met this criterion, there were serious problems with the data. The data of Figures 12, 13, and 14 also allowed identification of elements which were consistently good except for one error exceeding ±10 percent. A possible error in the flow estimation, the trace element concentration, data recording, etc., could be suspected. Table 37 data indicate that serious material imbalances were present for iron, calcium, potassium, and sodium. This data was extremely surprising due to the quantity of these elements present and the fact that these elements were routinely analyzed in fly ash samples.

The elements which have material balances with ±10 percent for two of the three loops are summarized in Table 38 with their associated total flows. Together, they account for 60.9 percent of the total flow. Therefore, approximately 61 percent of the trace element flow had a material balance with ±10 percent for at least two and possibly three of the loops. Further analysis was done on iron, calcium, potassium, and sodium in an attempt to see if there was a higher percentage of trace element flow estimable. Since the total flows for tests one and eight were previously identified as suspect, the material balances for these four trace elements were calculated for tests 2 through 7 to see if the fluctuations of tests 1 and 8 were the major problem. Table 39 summaries the results; and, as can be seen by comparison with Table 37, tests 1 and 8 flows were not the problem with these four elements. This comparison suggests a possible problem with flow estimation in general.

Special Considerations and Assumptions

Several topics and problem areas which occurred during the test program and must be identified and considered when interpreting the results.

TABLE 38. TRACE ELEMENTS WITH GOOD[1] MATERIAL BALANCES

Element	Total Flow (lb/h)	% Pulverizer Error	% Boiler Error	% ESP Error
Si	31,212.0	-6.6	+1.4	-4.4
Al	15,416.0	+5.5	-3.5	-9.0
Mg	852.2	+3.0	-0.5	+6.9
Ti	748.5	-7.0	+16.6	-7.1
Ba	98.0	-3.8	+49.5	-4.3
V	74.7	+3.4	+4.7	-12.0
Pb	23.4	-2.1	-42.6	-4.6
Cu	8.6	+59.1	-0.7	+3.7
Sb	2.3	+8.5	+3.7	-4.7
Be	1.4	-1.7	+9.6	-11.9

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[1] Error within ±10% for two of three loops.

TABLE 39. ANALYSIS OF LARGE FLOW TRACE ELEMENTS WITH LARGE ERRORS DAYS 1 AND 8 FLOWS REMOVED

Element	% Pulverizer Error	% Boiler Error	% ESP Error
Fe	+21.3	-17.4	+32.8
Ca	-28.7	+9.3	+37.8
K	+48.4	-9.1	-14.1
Na	-45.1	+76.1	-17.0

Figure 15 is a schematic of the system from the entrance point of the whole coal to the exit point of the fly ash from the ESP. The legend on the graph indicates where the flow rate and concentration was measured during the 8-day program.

The Mechanical Collector

At the time of this study the mechanical collector was in place, but all of the vanes were removed. By examining Figure 15, it is seen that the fly ash exiting the boiler and entering the mechanical collector was not sampled. It was assumed that the mechanical collector minus the vanes would remove an insignificant amount of material. A later analysis indicated that less than one-half of 1 percent of the daily flow through the mechanical collector was being collected.

Trace Element Flows

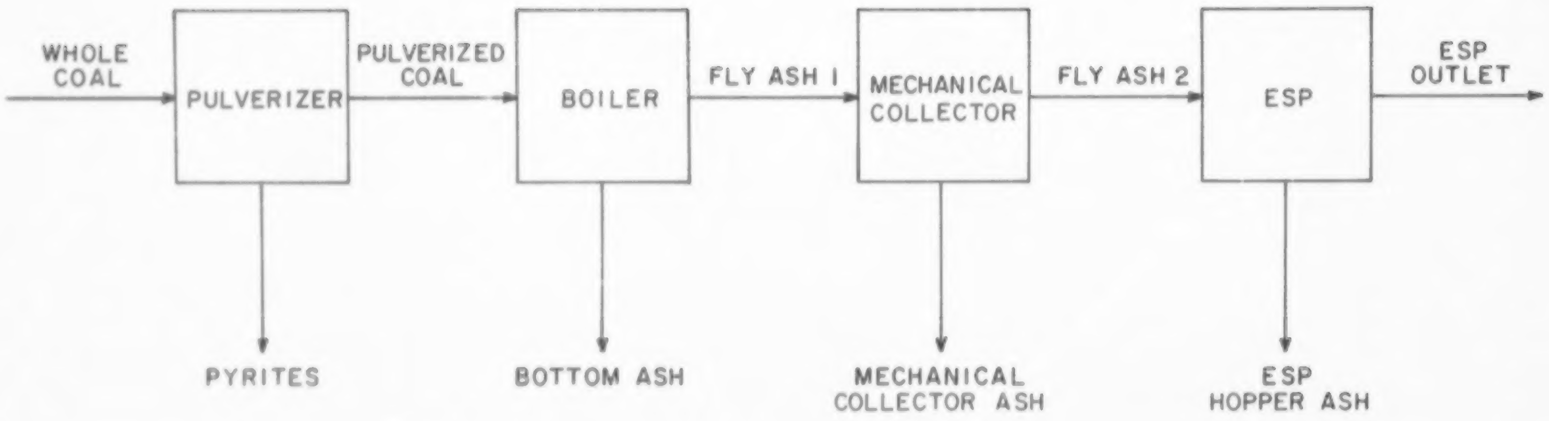
Some of the trace elements also had minimum detectability problems. Since the flows were small and measurable at most sample points, the following procedure was used to generate flows in order that a material balance could be approximated throughout the system: (1) the minimum detectable limit of the trace element was used as a maximum possible value for the interval from zero to that value; and (2) a random number was selected from that interval in such a way that every number in the interval had an equal chance of being selected. Table 40 lists the elements, the sample points, the tests where minimum detectable limits were encountered, and the "generated" value from the uniform random number generator.

Vapor Phase Data

Sampling took place at the inlet and outlet of the ESP. Due to the minute amount of material in the vapor phase, the collection took place over the first week (identified as test 1) and the second week (identified as test 2). All of the element concentrations were below the detectable or measurable limits. Some of the upper limits were higher than the amount of element in the whole coal. For example, in the test 1 inlet data, chromium, nickel, and lead are indicated as having flows of 10.7 lb/h, 16.24 lb/h, and 10.4 lb/h, respectively, or less. The average flows of these elements in the whole coal were 2.48 lb/h, 1.28 lb/h, and 2.93 lb/h, respectively. This data indicates that another approach to sampling the vapor phase needs to be examined.

Flow Rate Estimation and Associated Problems

The material flow rate was measured at the whole coal, the pyrites were measured from the pulverizer, and the solids were measured from the ESP (hopper and gas) outlets. The remaining flow rates were estimated. Table 41 summarizes the total material flows and contains an empirical


WHOLE COAL
PULVERIZER
PULVERIZED COAL
BOILER
FLY ASH 1
MECHANICAL COLLECTOR
FLY ASH 2
ESP
ESP OUTLET
PYRITES
BOTTOM ASH
MECHANICAL COLLECTOR ASH
ESP HOPPER ASH

SAMPLE POINT	CONCENTRATION	FLOWRATE
WHOLE COAL	MEASURED	MEASURED
PYRITES	MEASURED	MEASURED
PULVERIZED COAL	MEASURED	E[1]
BOTTOM ASH	MEASURED	E
FLY ASH 1	N[2]	N
MECHANICAL COLLECTOR ASH	N	N
FLY ASH 2	MEASURED	E
ESP HOPPER ASH	MEASURED	E
ESP OUTLET	MEASURED	MEASURED

[1] ESTIMATED

[2] NOT MEASURED OR ESTIMATED AT TIME OF STUDY

Figure 15. Simplified system schematic.

TABLE 40. TRACE ELEMENTS WITH MINIMUM DETECTABLE LIMITS

Element	Sample Point	Test	Limit (lb/h)	Generated Value
Ba	Whole Coal	4	6.60	1.33
Ba	Whole Coal	5	6.90	1.68
Ba	Whole Coal	6	6.60	2.47
Cd	Whole Coal	1	0.64	0.37
Cd	Whole Coal	2	0.66	0.23
Cd	Whole Coal	3	0.72	0.51
Cd	Whole Coal	4	0.67	0.14
Cd	Whole Coal	5	0.70	0.17
Cd	Whole Coal	6	0.67	0.66
Cd	Whole Coal	7	0.70	0.30
Cd	Whole Coal	8	0.66	0.28
Cd	Pulverized Coal	1	0.13	0.13
Cd	Pulverized Coal	2	0.13	0.04
Cd	Pulverized Coal	3	0.14	0.14
Cd	Pulverized Coal	4	0.13	0.04
Cd	Pulverized Coal	5	0.14	0.05
Cd	Pulverized Coal	6	0.13	0.12
Cd	Pulverized Coal	7	0.14	0.13
Cd	Pulverized Coal	8	0.13	0.06
Cd	Bottom Ash	1	0.003	0.001
Cd	Bottom Ash	2	0.004	0.003
Cd	Bottom Ash	3	0.005	0.002
Cd	Bottom Ash	4	0.005	0.004
Cd	Bottom Ash	5	0.005	0.003
Cd	Bottom Ash	6	0.004	0.001
Cd	Bottom Ash	7	0.006	0.004
Cd	Bottom Ash	8	0.005	0.002
Co	Whole Coal	1	0.64	0.31
Co	Whole Coal	2	0.66	0.59
Co	Whole Coal	3	0.72	0.10
Co	Whole Coal	4	0.67	0.61
Co	Whole Coal	5	0.70	0.36
Co	Whole Coal	6	0.67	0.48
Co	Whole Coal	7	0.70	0.19
Co	Whole Coal	8	0.66	0.30
F	Bottom Ash	1	0.017	0.010
F	Bottom Ash	2	0.022	0.021
F	Bottom Ash	3	0.024	0.018
F	Bottom Ash	4	0.024	0.013
F	Bottom Ash	5	0.025	0.007
F	Bottom Ash	6	0.021	0.002
F	Bottom Ash	7	0.031	0.029
F	Bottom Ash	8	0.026	0.003

TABLE 41. FLOW RATES AND ASSOCIATED ERRORS

Sample Point	Test	Flow Rate	Units of Flow Rate	Estimated Error
Whole Coal	1	64.4	t/h	±1.5 t/h
	2	65.9	t/h	±1.5 t/h
	3	72.1	t/h	±1.5 t/h
	4	66.8	t/h	±1.5 t/h
	5	69.7	t/h	±1.5 t/h
	6	66.9	t/h	±1.5 t/h
	7	69.9	t/h	±1.5 t/h
	8	66.2	t/h	±1.5 t/h
Pyrites	1	400	lb/h	±15 lb/h
	2	600	lb/h	±15 lb/h
	3	400	lb/h	±15 lb/h
	4	400	lb/h	±15 lb/h
	5	600	lb/h	±15 lb/h
	6	600	lb/h	±15 lb/h
	7	400	lb/h	±15 lb/h
	8	400	lb/h	±15 lb/h
ESP Outlet	1	501	lb/h	±20 lb/h
	2	1,168	lb/h	±20 lb/h
	3	762	lb/h	±20 lb/h
	4	856	lb/h	±20 lb/h
	5	2,752	lb/h	±20 lb/h
	6	387	lb/h	±20 lb/h
	7	318	lb/h	±20 lb/h
	8	386	lb/h	±20 lb/h

estimate of the error associated with the flows. Since two of the three flows around the pulverizer were measured, the mass balance around the pulverizer was the best. The lack of measured flow rates resulted in the boiler and ESP having larger mass imbalances. The trace elements constitute only a small part of the total mass flow: of the 68 tons of whole coal per day on the average, only about 5 tons are trace elements; of approximately 500 lb/day in the pyrites, 140 lb (28 per-cent) are trace elements; of the 890 lb/day at the ESP outlet, 225 lb (25.3 percent) are trace elements. After taking the natural variability of the coal and the detection limits of the instruments used to measure trace elements, the variability of the resulting data was understandable. The factors that can reduce variability are more frequently measured flow rates around the boiler and ESP and, when possible, the use of better instruments and sampling procedures.

In examining the trace element data, one omission stood out--the lack of sulfur data. It is strongly recommended that sulfur be included with Fe and Al as an element to be monitored since the chemistry and behavior characteristics of these elements are available as checks on total system behavior, flow rates, and accuracy.

ESTIMATE OF THE MASS BALANCE

In estimating the mass balance of the trace elements, several assumptions were made. First, vapor phase estimates were not made for all elements due to the lack of reliable and quantitative information on the vapor phase. While the total mass of the elements in the vapor phase is small when compared to the total mass balance, it is recognized that the vapor phase is an area of concern. Second, for ease of computation, the total trace element flow was set to a standard of 10,000 lb/h in the whole coal. Third, for each individual element the most reasonable flows were chosen or estimated for consistency throughout the system. While this was an empirical judgment, it represented the best estimate possible.

Table 42 displays the estimated mass balance by sample points summed over all 25 elements and shows the percentage breakdown of the flows. Table 43 presents the estimated mass balance by element at each sample point. Particularly difficult elements to estimate are identified.

TABLE 42. ESTIMATED MASS BALANCE OF MAJOR AND TRACE ELEMENTS (SUMMATION OF 25 ELEMENTS) BY SAMPLE POINTS

	Flow (lb/h)	% of Loop Input	Input
Whole Coal	10,000.000		
Pyrites	153.730	1.5373	Whole Coal
Pulverized Coal	9,846.27	98.4627	Whole Coal
Bottom Ash	2,302.317	23.3826	Pulverized Coal
Vapor Phase[1]	219.10	2.2252	Pulverized Coal
ESP Inlet	7,324.853	74.3922	Pulverized Coal
ESP Hopper	7,049.853	96.2457	ESP Inlet
ESP Outlet	275.000	3.7543	ESP Inlet

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[1] The vapor phase was approximated by adding the chlorine and fluorine material loss exiting the boiler.

TABLE 43. ESTIMATED MASS BALANCE BY ELEMENT FOR EACH SAMPLE POINT[1]

Element	Whole Coal (lb/h)	Pyrites (lb/h)	Pulverized Coal (lb/h)	Bottom Ash (lb/h)	Inlet (lb/h)	ESP Hopper (lb/h)	Outlet (lb/h)
Al	1960.000	10.000	1950.000	430.000	1520.000	1473.250	46.750
As	1.500	.050	1.450	.050	1.400	1.100	.300
Ba	14.000	.200	13.800	4.000	9.800	9.750	.050
Be	.170	.001	.1690	.029	.1400	.139	.001
Ca	625.000	3.500	621.500	69.000	552.500	539.000	13.500
Cd	.330	.001	.329	.002	.327	.287	.040
Cl[2]	220.000	.040	219.960	.150	8.650	1.150	7.500
Co	.360	.020	.340	.230	.110	.100	.010
Cr	2.500	.030	2.470	.670	1.800	1.770	.030
Cu	.800	.020	.780	.280	.500	.300	.200
F[2]	12.000	.030	11.970	.030	4.000	3.000	1.000
Fe	2645.000	115.711	2529.289	947.780	1581.509	1518.259	63.250
Hg	.040	0.000	.040	0.000	.040	.010	.03
K	330.000	2.200	327.800	75.000	252.800	250.800	2.000
Mg	110.000	0.800	109.200	22.200	87.000	84.400	2.600
Mn	5.500	.090	5.410	1.410	4.000	3.400	0.600
Na	85.000	.250	84.750	14.750	70.000	68.000	2.000
Ni	1.500	.030	1.470	.470	1.000	.850	.150
Pb	3.000	.080	2.920	1.890	1.030	1.000	.030
Sb	.280	.001	.279	.020	.259	.199	.060
Se	.410	.006	.404	.003	.401	.396	.00
Si	3875.000	20.000	3855.000	713.103	3141.897	3007.843	134.05
Ti	90.000	0.500	89.500	18.750	70.750	70.500	.250
V	9.810	.070	9.740	1.800	7.940	7.850	.090
Zn	7.800	.100	7.700	.700	7.000	6.500	.500

---

[1] The vapor phase is assumed to be 219.10 lb/h.

[2] Element's mass balance particularly difficult to estimate based on data because large amounts are known to escape in the vapor phase.

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Appendix A

DESCRIPTION OF SAMPLING TRAINS

DESCRIPTION OF SAMPLING TRAINS

Train 1 - Total Particulate

A schematic of this train is depicted in Figure A-1. Basically, this train is operated in the same manner as the EPA method 5 train. It traverses the gas stream and samples isokinetically. In this, as well as all other trains, 3.5-inch filter holders were used; and because of delay in the delivery of filter substrates from the vendor, Gelman AE-type filters were used instead of the intended Spectro Grade filters. Simultaneous measurements of total particulate concentrations were carried out at the inlet and outlet of the ESP. One sampling run of 1-4 hours was made each day at each of these locations. A total of eight samples were taken at each location for the entire study.

Train 2 - Vapor-Phase Trace Elements

Figure A-2 shows a schematic of this train, which also served as a backup train for Hg. In contrast to train 1, train 2 operates at a proportional flow rate and at a fixed point in the flue duct. The K_2CO_3 solution was used to collect Se, HCl, and HF, as well as to neutralize SO_2. The KOH solution was used to capture Sb and As, and to scrub-out SO_2. The strong oxidizing solutions containing mixtures of H_2O_2, HNO_3, and $AgNO_3$ served to absorb Sb and As as well as the remaining elements listed above. The lower ends of the bubbler tubes in impingers 1, 2, and 3 were made of fritted glass with pore sizes of 100 µm to increase the gas-liquid contact and to enhance the collection efficiencies of the impingers.

During the sampling, the strengths of the K_2CO_3 in impinger 1 and of the H_2O_2 solutions in impingers 5 and 6 were checked by running parallel sampling with identical impingers containing K_2CO_3 and mixtures of H_2O_2, HNO_3, and $AgNO_3$, respectively. The strength of K_2CO_3 was determined by titration against H_2SO_4 to the phenolphthalein end point, and that of H_2O_2 by titration against $KMnO_4$. The absorbing solutions were replenished whenever necessary to maintain at least a 50-percent excess.

Sampling was done simultaneously at the inlet and outlet of the ESP. Preliminary studies indicated there were small concentrations of trace elements present in the gases. The original plans for collecting 4-hour samples in the morning and the afternoon were abandoned in favor of running the trains continuously for four or five days. A total of two samples were collected at the inlet and outlet of the ESP, respectively.

Train 3 - Particulate Interference

This train, as depicted in Figure A-3, is a modification of the original train which had been intended for use in determining the interference of fine particle penetration on the vapor-phase trace elements collected by trains 2 and 4. The original train contained two particulate filters; one was a 0.3-µm fiberglass filter in front of the condenser-ice

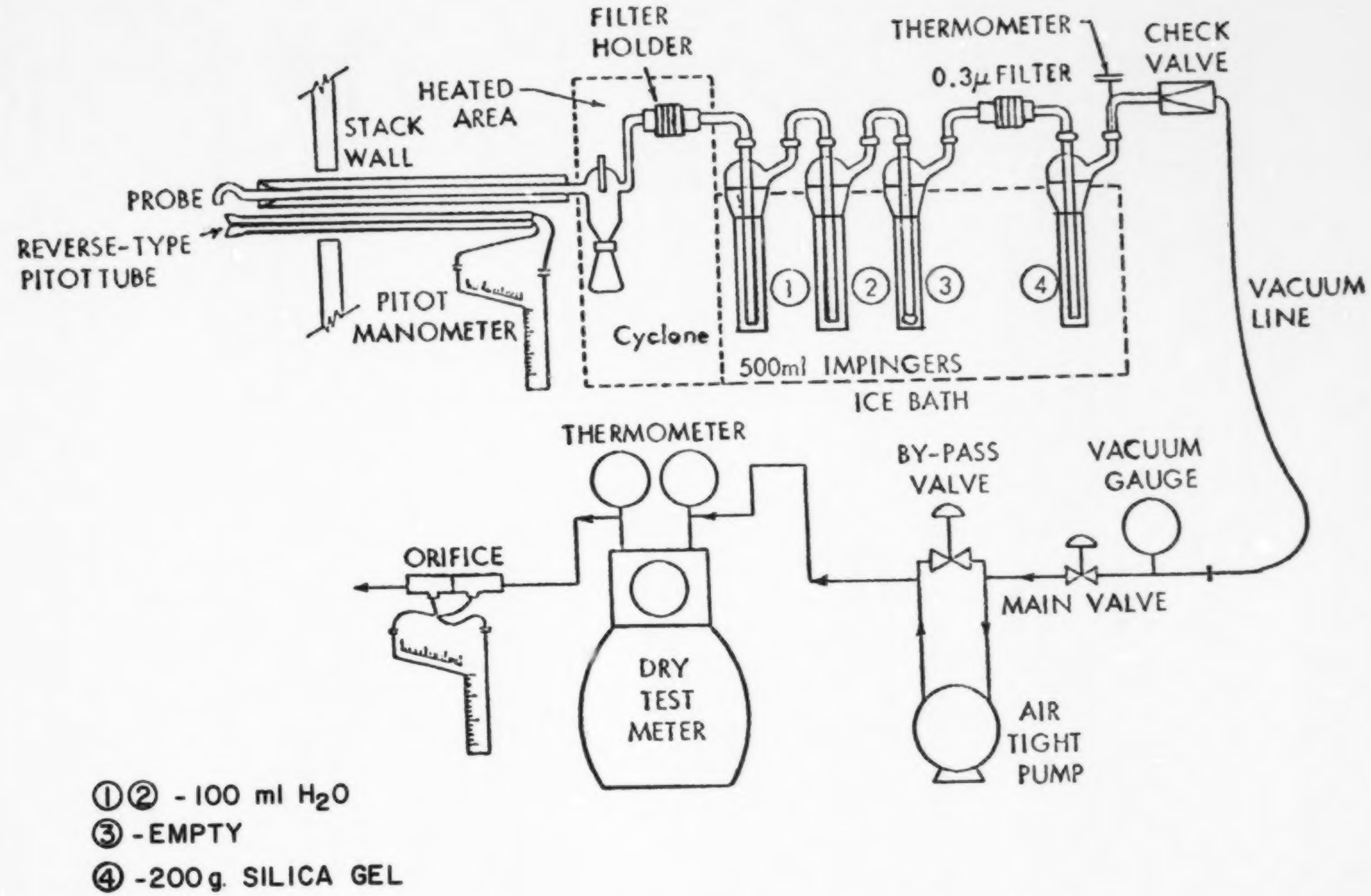
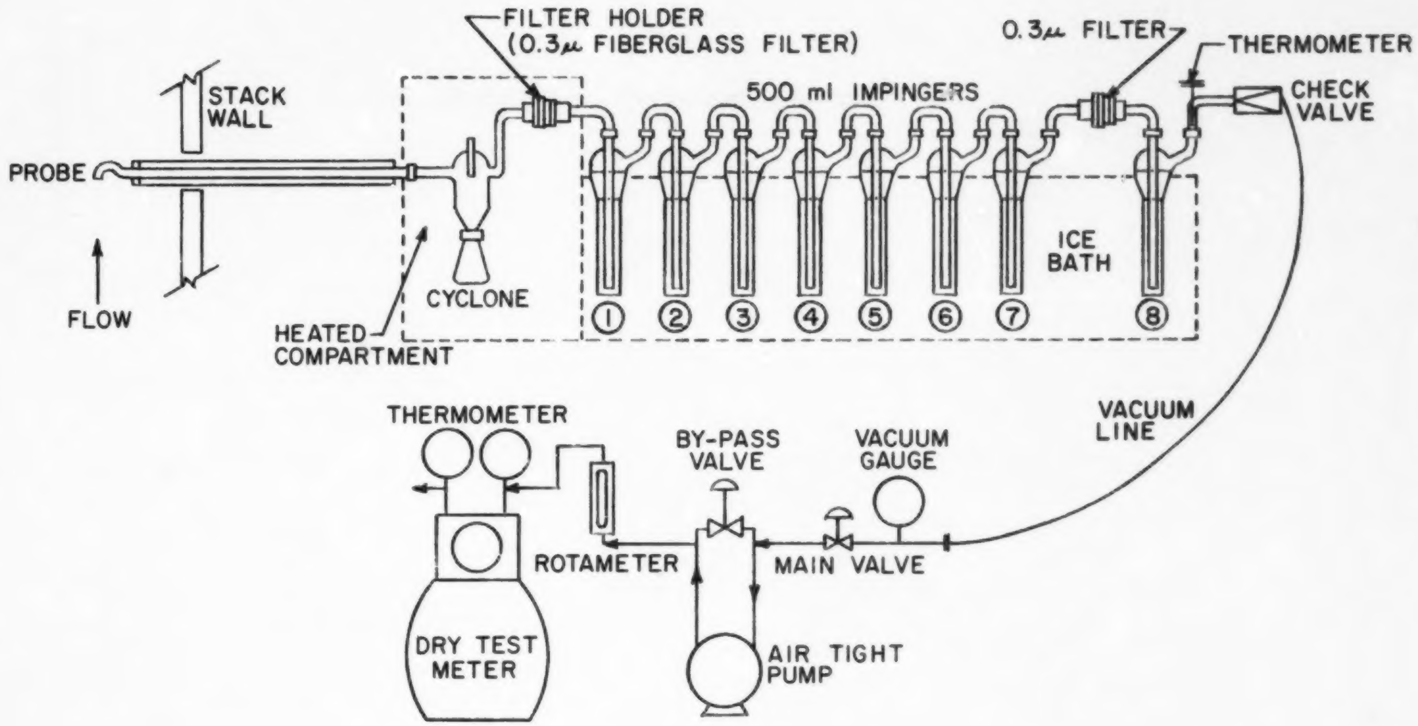

FILTER HOLDER
HEATED AREA
STACK WALL
PROBE
REVERSE-TYPE PITOT TUBE
PITOT MANOMETER
Cyclone
THERMOMETER
0.3μ FILTER
CHECK VALVE
①
②
③
④
500ml IMPINGERS
ICE BATH
VACUUM LINE
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
ORIFICE
DRY TEST METER
AIR TIGHT PUMP
①② - 100 ml H_2O
③ - EMPTY
④ - 200 g. SILICA GEL

Figure A-1. Total particulate train.


FILTER HOLDER
(0.3μ FIBERGLASS FILTER)
0.3μ FILTER
THERMOMETER
STACK WALL
500 ml IMPINGERS
CHECK VALVE
PROBE
FLOW
CYCLONE
HEATED COMPARTMENT
ICE BATH
① ② ③ ④ ⑤ ⑥ ⑦ ⑧
VACUUM LINE
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
ROTAMETER
MAIN VALVE
DRY TEST METER
AIR TIGHT PUMP

①- 200 ml, 10% K_2CO_3 (WEIGHT/VOLUME)
②③- 200 ml, 1M KOH
④⑦- EMPTY
⑤⑥- 250 ml, ($2MH_2O_2 + 0.2MHNO_3 + 0.02M AgNO_3$)

Figure A-2. Vapor-phase, trace-element train.

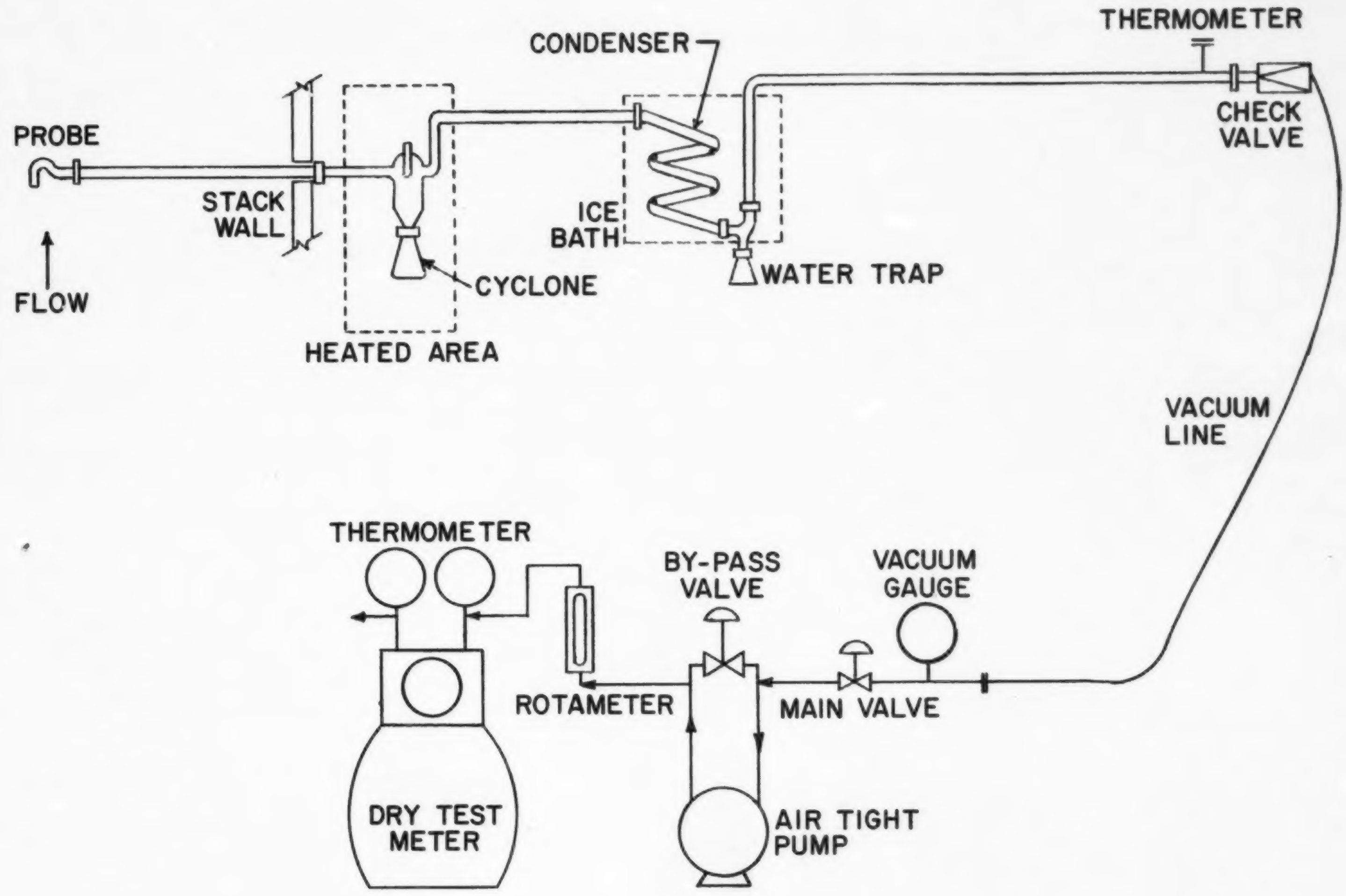

THERMOMETER
CONDENSER
PROBE
CHECK VALVE
STACK WALL
ICE BATH
FLOW
CYCLONE
WATER TRAP
HEATED AREA
VACUUM LINE
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
ROTAMETER
MAIN VALVE
DRY TEST METER
AIR TIGHT PUMP

Figure A-3. Particulate interference sampler train.

bath. As a result of the difficulties encountered with these filters during the preliminary tests, the decision was made to eliminate the membrane filter entirely and to replace the fiberglass filter with a cyclone collector. Glass wools were packed in the outlet portion of the cyclone to capture Si, Na, and K that may have penetrated the cyclone collector. This train was run at the inlet duct.

Train 4 - Mercury/Backup Vapor-Phase Trace Elements

This train is shown schematically in Figure A-4. The strong oxidizing solutions of $KMnO_4$ are effective absorbers for Hg. Impinger 1 is identical to impinger 1 used in train 2. Simultaneous sampling was done at the inlet and outlet of the ESP. Two runs were made each day: one in the morning and one in the afternoon. A total of eight samples were collected at each of the two sampling locations.

Three separate solutions were retained for samples collected from this train. The first was the catch in the K_2CO_3 solution from impinger 1. The second was the combined catch from the $KMnO_4$ and HNO_3 solutions in impingers 2-5. The third was the solution obtained from rinsing impingers 2-5 with 10-percent oxalic acid solution.

Brink Cascade Impactor

Figure A-5 is a schematic illustration of the BSM11, 5-stage Brink impactor for particle size classification. Because of its lower gas sampling flow rate and larger capacity, the Brink impactor was used at the ESP inlet. Teflon and aluminum substrates were used with the stages, but Teflon was found to be a very poor collection substrate during preliminary tests. Final tests were conducted using aluminum substrates.

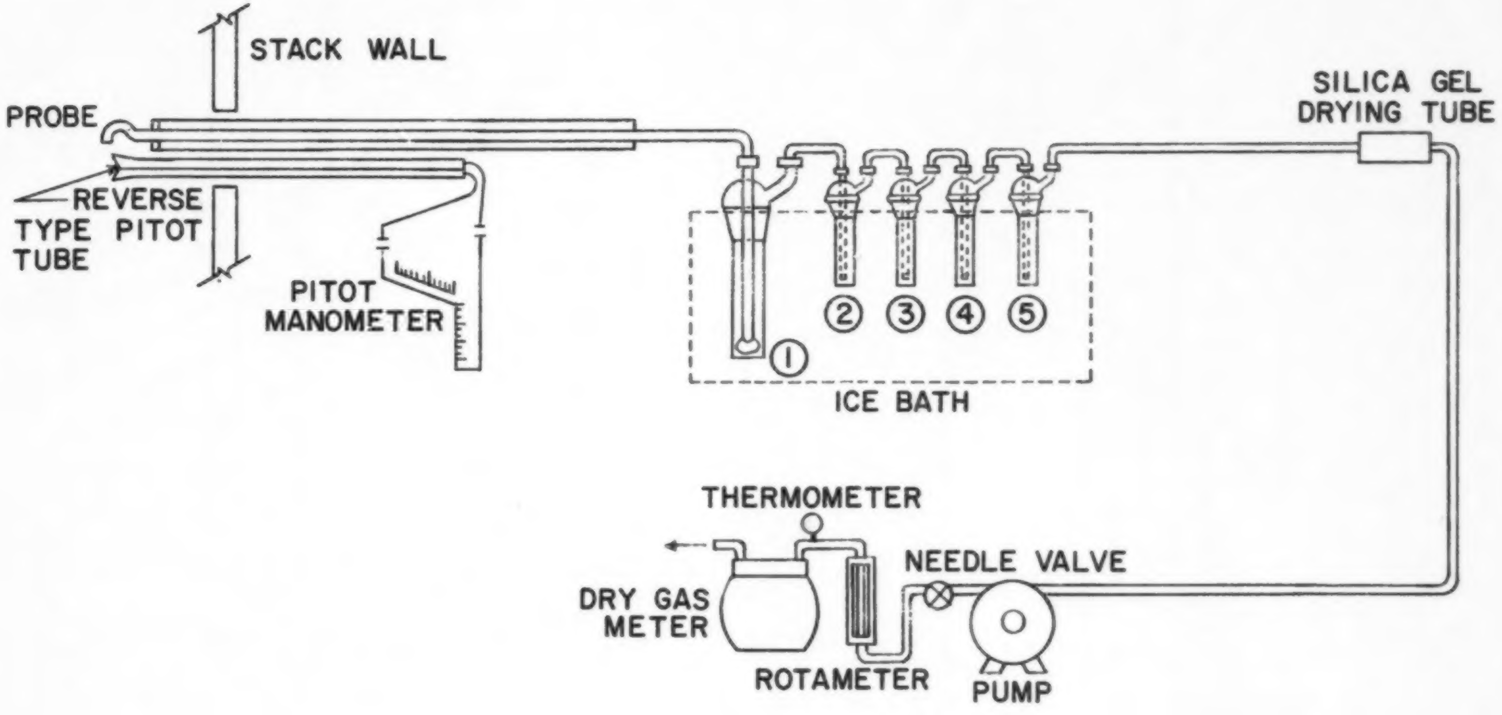
Runs of 2.5 to 7 minutes were made with the impactor in the morning and again in the afternoon during each sampling day. The impactor was inserted to a depth of five feet into the duct, and the sampling rate was adjusted to achieve isokinetic sampling from an experimentally predetermined flue gas velocity at that point.

Andersen Cascade Impactor

Figure A-6 shows a schematic diagram of the Andersen system. Because of its higher volume flow rate, this impactor was used at the ESP outlet to obtain size distribution information. Fiberglass filters were used as substrate. The sampling procedure used was identical to that followed for the Brink Cascade Impactor. Test runs lasted from 37 to 360 minutes.

Optical and Diffusional Sizing System

An optical particle counter (Climet) and a diffusion battery (Thermo Systems, Inc.), coupled with a condensation nuclei counter (General Electric), were used to measure the number, concentration, and size distribution of particulates in the size range from 0.02 μm up to 20 μm. A special


STACK WALL
PROBE
REVERSE TYPE PITOT TUBE
PITOT MANOMETER
①
② ③ ④ ⑤
ICE BATH
SILICA GEL DRYING TUBE
THERMOMETER
NEEDLE VALVE
DRY GAS METER
ROTAMETER
PUMP

①-200 ml, 10% K_2CO_3 (WEIGHT/VOLUME)
②③④- 20 ml, (3% $KMnO_4$ + 14.3% HNO_3)
⑤-EMPTY

Figure A-4. Mercury train/back-up for vapor-phase trace elements.

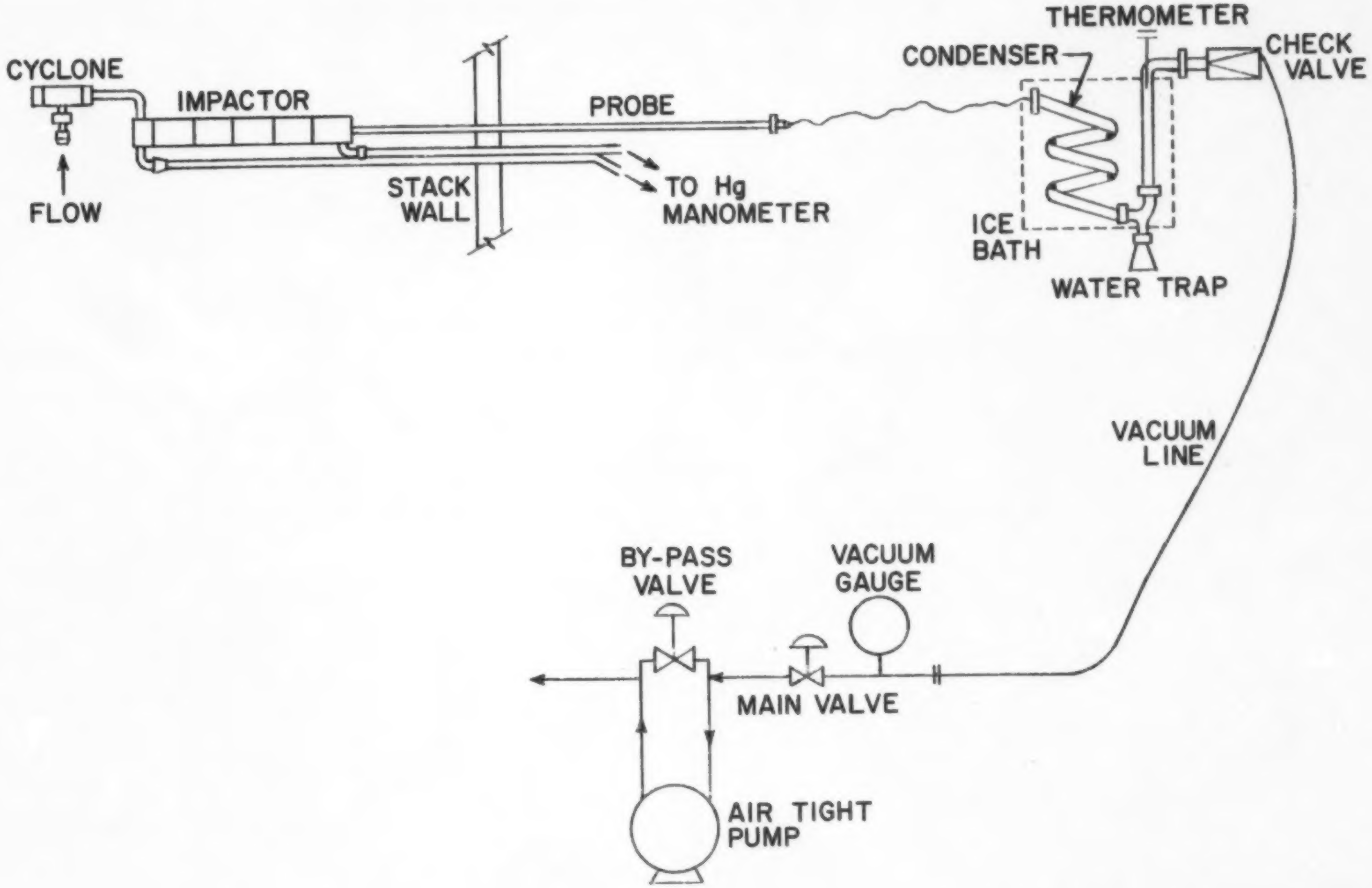
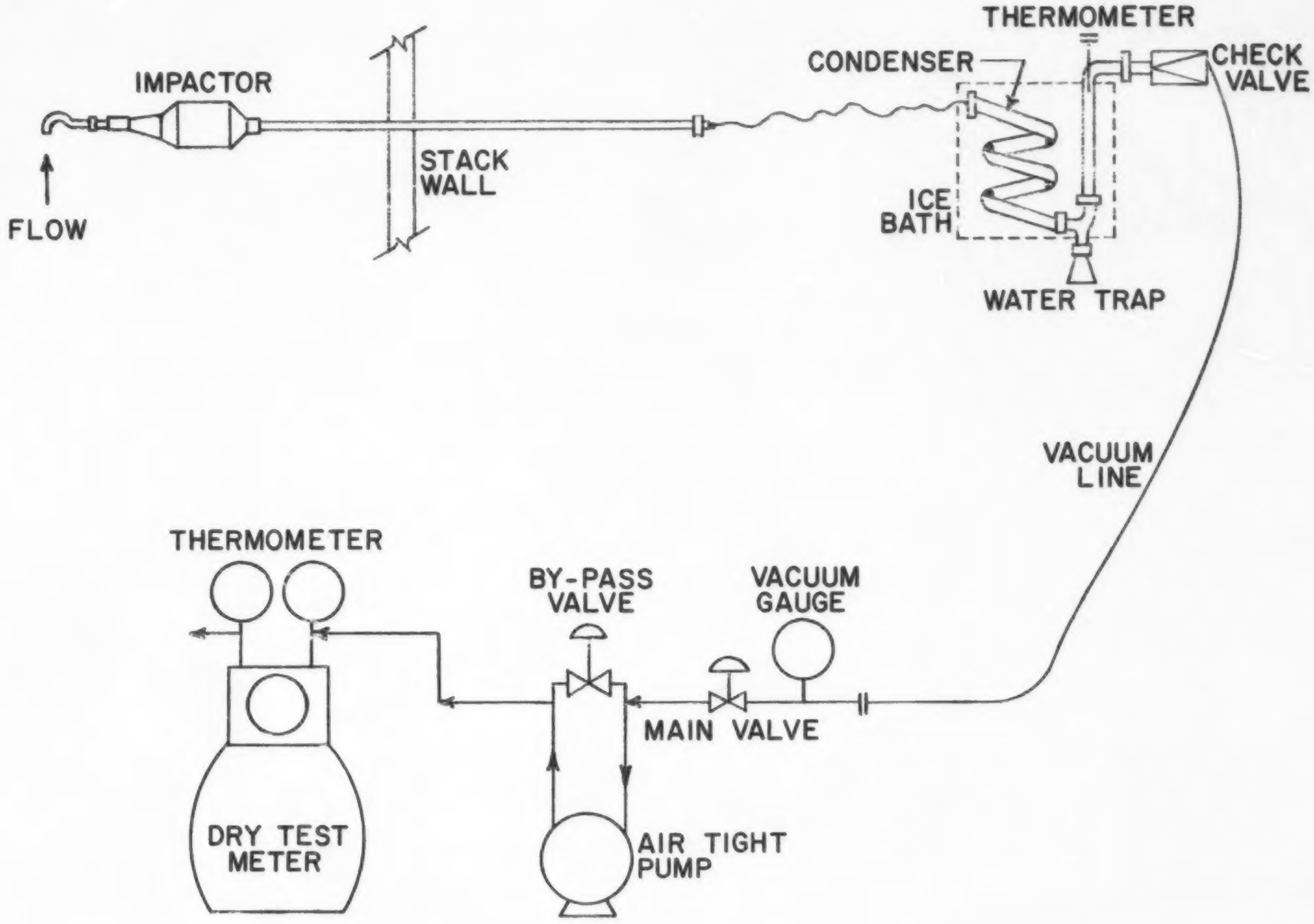

CYCLONE
FLOW
IMPACTOR
STACK WALL
PROBE
TO Hg MANOMETER
CONDENSER
THERMOMETER
CHECK VALVE
ICE BATH
WATER TRAP
VACUUM LINE
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
AIR TIGHT PUMP

Figure A-5. Brink cascade impactor sampling train.



THERMOMETER
IMPACTOR
CONDENSER
CHECK VALVE
STACK WALL
ICE BATH
FLOW
WATER TRAP
VACUUM LINE
THERMOMETER
BY-PASS VALVE
VACUUM GAUGE
MAIN VALVE
DRY TEST METER
AIR TIGHT PUMP

Figure A-6. Andersen impactor sampling train.

instack sample dilution system was designed by MRI for use with this particle measurement system. The sample dilution was affected by the injection of high-pressure clean air into one end of the dilution chamber which was inserted in the stack. The vacuum created by the high-pressure air jet drew flue gas into the chamber through a nozzle into a cyclone; and the flue gas was diluted 50-fold in the chamber by the high-pressure air before it could reach the sample probe of the optical and diffusional sizing system. Figure 11 is a schematic of this sampling system.

Measurements were made alternately at the inlet and outlet ducts of the ESP. Malfunction of the vacuum pump for the optical particle counter reduced the number of runs that could be made with this instrument. Four inlet and four outlet runs were conducted using the Climet optical counter. Seven inlet and seven outlet runs were conducted using the diffusion battery-condensation nuclei counter system.

Polycyclic Organic Material (POM) Sampling System

The POM system consists of a standard EPA Method 5 train modified to include a Tenax adsorbent sampling system between the filter and the impingers (Figure A-7). In operation, the stact gas is sampled isokinetically by a sampling probe and passed through a heated filter. It then passes into the cooling coil of the Tenax adsorbent sampler, up through a Pyrex frit, and into the Tenax column. The cooling coil and Tenax adsorbent are maintained at about 60°C by means of a thermostatically controlled bath. The gas leaving the sampler goes through an aqueous impinger, a Drierite trap, and a dry gas meter. At the conclusion of the run, the adsorbent sampler is sealed and stored in darkness for subsequent solvent extraction of the POM's.

Because of physical limitations, POM's were sampled through ports on the adjacent inlet and outlet ducts of the ESP instead of the same ducts being used for other samples. A total of three complete runs was made--two at the outlet and one at the inlet of the ESP. Each sampling run lasted for about 8 to 10 hours.

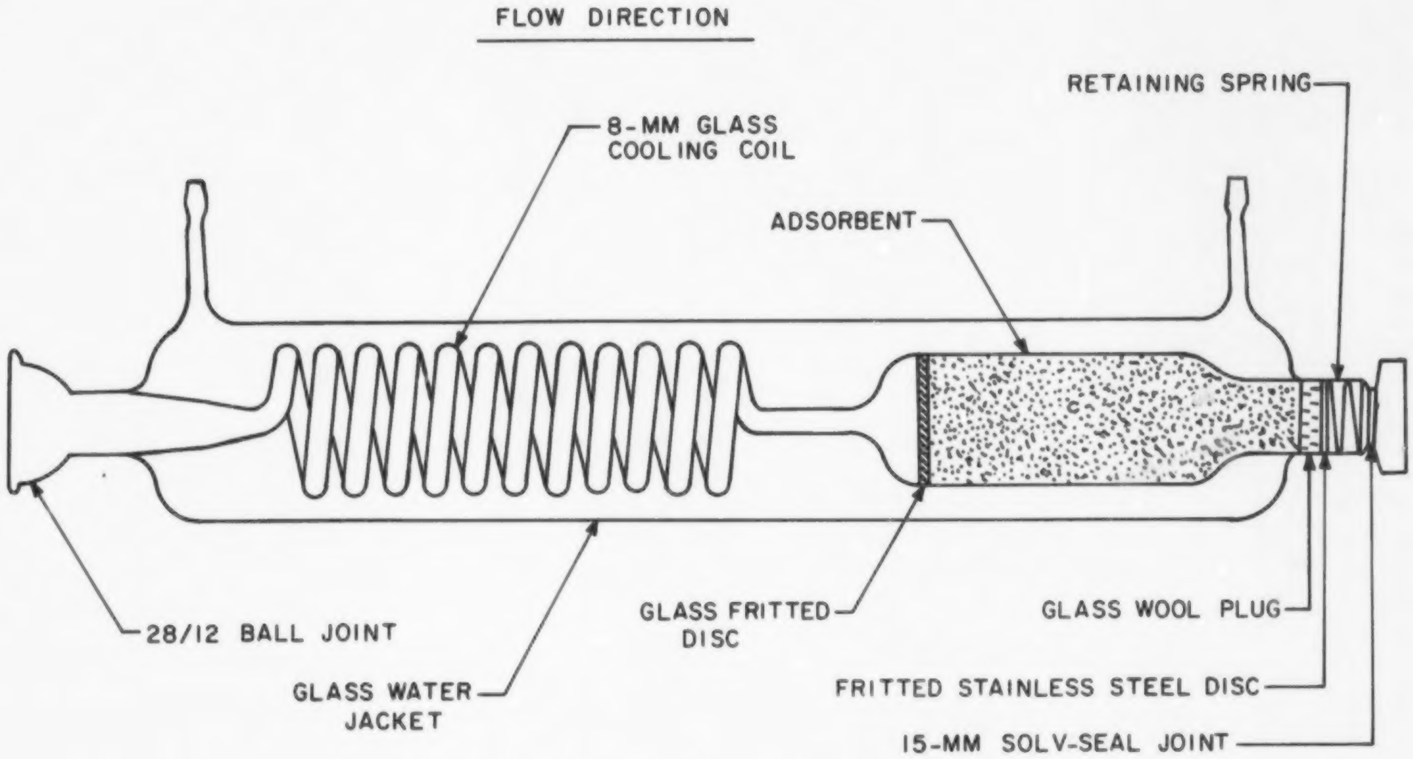

FLOW DIRECTION
RETAINING SPRING
8-MM GLASS COOLING COIL
ADSORBENT
28/12 BALL JOINT
GLASS WATER JACKET
GLASS FRITTED DISC
GLASS WOOL PLUG
FRITTED STAINLESS STEEL DISC
15-MM SOLV-SEAL JOINT

Figure A-7. POM sample system.

Appendix B

METHODS OF CHEMICAL ANALYSIS

METHODS OF CHEMICAL ANALYSIS

1. Analytical Procedures for Coal

1.a Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, V, and Zn in coal

1.b Al, Ba, Cd, Co, Na, and Si in coal

1.c As in coal

1.d Se and Sb in coal

1.e Cl in coal

1.f F in coal

1.g Hg in coal

2. Analytical Procedures for Particulate and Impinger Water from Train 1 Inlet to ESP

2.a Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, V, and Zn in particulate

2.b Al, Ba, Cd, Co, and Na in particulate

2.c As in particulate

2.d Se and Sb in particulate

2.e Cl in particulate

2.f F in particulate

2.g Hg in particulate

2.h Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn in impinger water

2.i As in impinger water

2.j Cl in impinger water

2.k F in impinger water

2.l Se and Sb in impinger water

2.m Si in impinger water

3. Analytical Procedures for Particulate and Impinger Water from Train 1 Outlet to ESP

3.a Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Ni, Pb, Sb, Se, Ti, V, and Zn in particulate

3.b Cl and F in particulate

3.c Impinger water

4. Analytical Procedures for Vaporous Phase Trace Elements from Train 2

4.a Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn in K_2CO_3 or KOH matrix

4.b As and Sb in K_2CO_3 or KOH matrix

4.c Cl and F in K_2CO_3 or KOH matrix

4.d Se in K_2CO_3 or KOH matrix

4.e Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn in H_2O_2 matrix

4.f As and Sb in H_2O_2 matrix

4.g Cl and F in H_2O_2 matrix

4.h Se in H_2O_2 matrix

4.i Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ti, V, and Zn in H_2SO_4 matrix

4.j Pb and Ni in H_2SO_4 matrix

4.k As in H_2SO_4 matrix

4.1 Cl and F in H_2SO_4 matrix

4.m Se and Sb in H_2SO_4 matrix

5. Analytical Procedures for Mercury from Train 4

5.a Hg in K_2CO_3 matrix

5.b Hg in $KMnO_4$ matrix

5.c Hg in oxalic acid rinse

6. Analytical Procedures for Particulate from the Brink Impactor

6.a Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Ti, V, and Zn in particulate

6.b Cl and F in particulate

7. Analytical Procedures for Particulate from the Andersen Impactor

7.a Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Ti, V, and Zn in particulate

7.b Cl and F in particulate

8. Analytical Procedures for ESP Hopper Ash

METHODS OF CHEMICAL ANALYSIS FOR TEST SAMPLES

Eight analytical instrumental methods, as shown in Table B-1, were used for the chemical analysis of the collected samples. The procedures for analyzing samples were selected by TVA's laboratory according to sample size and sample matrix. One test run of fine particulate sample collected with the Brink and Andersen Impactors was analyzed by Accu-Lab, Inc., by Spark Source Mass Spectrometry.

Coal and particulate (total particulate train at the precipitator inlet, ESP hopper ash) samples had to be converted to solution for chemical analysis. They were subjected to acid or base dissolution, lithium metaborate fusion, or Eschka digestion followed by acid dissolution. Exceptions were the Train 1 inlet, Andersen and Brink impactor samples, in which ethanol was used to dislodge the elements from the substrates prior to dissolution by a mixture of hydrofluoric and perchloric acids. Identical treatment of the substrate was made to obtain a background correction.

Because of the extremely small quantity of particulate collected in the probe of the total particulate train at the precipitator outlet, collected on the Brink impactor pans, and collected on the post-ESP filter substrate associated with the total particulate train and Andersen impactor, microchemical techniques were employed in analyzing these samples.

Liquid samples (such as KOH, K_2CO_3, $KMnO_4$, and impinger water) were treated with either acid or oxidizing reagents before chemical analysis. Other liquid samples (such as H_2O_2, H_2SO_4 or theoxalic acid rinse), were diluted with reagent water and analyzed, directly analyzed, acidified, or treated with oxidants prior to chemical analysis.

1. Analysis Procedure for Coal

The coal was removed from the sealed container, oven-dried at 40°C for 16 hours, and air-dried for 2 hours. The sample was then ground to pass through a No. 60 mesh before being ashed or digested.[2]

Figure B-1 depicts the analytical procedure for the determination of trace elements in coal. As shown, the coal was ashed and then digested for the determination of Be, Cr, Cu, K, V, Zn, Ca, Fe, Mg, Mn, Ti, Ni, and Pb. The coal was digested for the determination of Si, Al, Ba, Cd, Co, Na, As, Se, Sb, Cl, F, and Hg.

Five grams of the coal sample were accurately weighed into a porcelain dish and placed in a cold muffle furnace. The furnace was heated to a temperature of 300°C for one hour and then increased to 500°C for two hours. The ash was stirred and heated until all carbonaceous material disappeared. The sample was cooled and ground in an agate mortar. The coal was reignited at 500°C for one hour, cooled rapidly, and weighed immediately.[2]

TABLE B-1

METHODS OF CHEMICAL ANALYSIS

Type Sample	Coal	Train 1 Inlet	Train 1 Outlet	Train 1 Impunger Water Inlet & Outlet	Vapor Phase Train K_2CO_3 or KOH	 H_2O_2	 H_2SO_4	Mercury Train 2 Oxalic Acid 75 ml $KMnO_4$ 10 ml H_2CO_3 100 ml	Brink Impactor	Andersen Impactor	ESP Hopper Ash
Sample Size Required	10 Grams	3.5 Grams	0.1 Grams	105 mls	200 mls	200 mls	200 mls		1 mg	10 mg	
Inductively Coupled Argon Plasma Atomic Emission Spectroscopy	Be,Ca,Cr Cu,Fe,K Mg,Mn,Ni Pb,Si,Ti V,Zn	Be,Ca,Cr Cu,Fe,K Mg,Mn,Ni Pb,Si,Ti V,Zn	Al,As,Ba,Be Ca,Cu,Co,Cr Fe,K,Mg,Mn Ni,Sb,Ti,V Zn	Al,Ba,Be Ca,Cd,Co,Cr Fe,Mg,Mn,Ni Pb,Ti,V,Zn	Al,Ba,Be Ca,Cd,Co,Cr Cu,Fe,Mg Mn,Ni,Pb Ti,V,Zn	Al,Ba,Be,Ca Cd,Co,Cr Cu,Fe,Mg Mn,Ni,Pb Ti,V,Zn	Al,Ba,Be Ca,Cd,Co Cr,Cu,Fe Mg,Mn,Ti V,Zn		Al,As,Ba,Be Ca,Co,Cr,Cu Fe,K,Mg,Mn Na,Ni,Sb Ti,V,Zn	Al,As,Ba,Be Ca,Co,Cr,Cu Fe,K,Mg,Mn Na,Ni,Sb Ti,V,Zn	Be,Ca,Cr Cu,Fe,K Mg,Mn,Ni Pb,Si,Ti V,Zn
Atomic Absorption	Al,As,Ba Cd,Co,Hg Na,Se,Sb	Al,As,Ba Cd,Co,Hg Na,Se,Sb	Hg,Se	As,Na,K Se,Sb,Se	As,Sb,Se	As,Sb,Se	As,Ni Pb,Sb,Se	Hg	Hg,Se	Hg,Se	Al,As,Ba Cd,Co,Hg Na,Sb,Se
Gravimetry						Cl					
Potentiometric Tritration	Cl	Cl		Cl	Cl		Cl				Cl
Ion Chromatography			CL,F						CL,F	Cl,F	
Specific Ion Electrode	F	F		F	F	F	F				F
Differential Pulse Anodic Stripping Voltametry			Cd,Pb						Cd,Pb	Cd,Pb	
Colorimetry				Si							

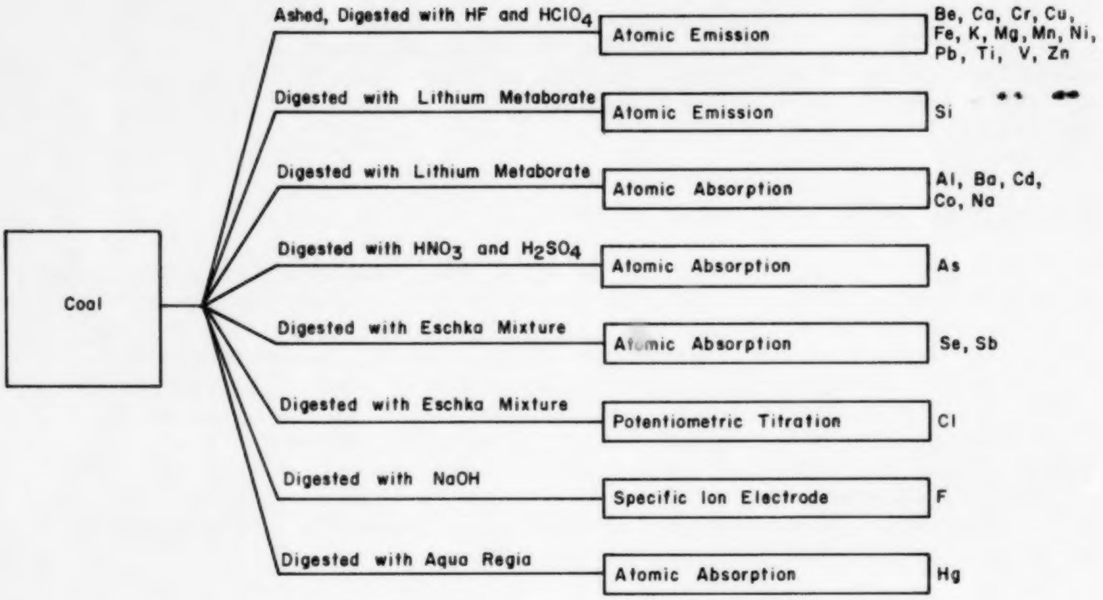

Coal
Ashed, Digested with HF and $HClO_4$
Atomic Emission
Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, V, Zn
Digested with Lithium Metaborate
Atomic Emission
Si
Digested with Lithium Metaborate
Atomic Absorption
Al, Ba, Cd, Co, Na
Digested with HNO_3 and H_2SO_4
Atomic Absorption
As
Digested with Eschka Mixture
Atomic Absorption
Se, Sb
Digested with Eschka Mixture
Potentiometric Titration
Cl
Digested with NaOH
Specific Ion Electrode
F
Digested with Aqua Regia
Atomic Absorption
Hg

Figure B-1. Analytical procedures for trace element analysis of coal

1.a Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, V, and Zn in Coal

A ground and weighed ash sample (approximately 0.05 grams) was placed in a 1-ml platinum crucible; and 0.5-ml Ultrex grade HF and 0.05-ml Ultrex grade $HClO_4$ were added. The mixture was heated to dryness at a temperature of 250°C. The evaporation was repeated twice with new portions of the acids. The residue was cooled and moistened with 0.05-ml Ultrex HCl and 0.5-ml deionized water. The mixture was covered and heated, without boiling, in a sand bath approximately 5 minutes until all salts were brought into solution. The solution was cooled, transferred to a volumetric flask, and made up to 5.0 ml with 5 percent Ultrex grade HCl.[2] A 1.5-2.0-ml aliquot of this solution was used to determine the concentration of Be, Cr, Cu, K, V, Zn, Ni, and Pb by atomic emission.[1] A 0.05-ml aliquot was diluted to 1.05 ml (21X) with five percent Ultrex HCl and used to determine the concentration of Ca, Fe, Mg, Mn, and Ti by atomic emission.[1]

1.b Al, Ba, Cd, Co, Na, and Si in Coal

A ground and weighed coal sample (0.5 grams) was mixed with 2.0 grams of reagent grade lithium metaborate in a platinum crucible and heated in a muffle furnace at 900°C until a clear melt was obtained. The mixture was cooled and placed in a beaker containing 8 ml of reagent grade HNO_3 and 150 ml of deionized water. The mixture was stirred vigorously until all material dissolved, and tartaric acid was added at a concentration of 1 percent. The solution was made up with deionized water in a volumetric flask[5] to a final volume of 250 ml. One aliquot of this solution was used to determine the concentration of Si by atomic emission.[1] A second aliquot of this solution was used to determine the concentrations of Al, Ba, Cd, Co, and Na by atomic absorption.[4]

1.c As in Coal

For the determination of As, an accurately weighed 0.5 g sample of ground coal was placed in a generating flask and mixed with 7.0 ml reagent grade (1 + 1) H_2SO_4 and 5.0 ml concentrated redistilled HNO_3, and was evaporated to SO_3 fumes.[11] The mixture was cooled, 25.0 ml of deionized water were added, and the evaporation procedure was repeated to expel oxides of nitrogen. The mixture was diluted to 100.0 ml with deionized water; and the arsenic was converted to the hydride by adding KI, $SnCl_2$ and powdered zinc.[12] The gaseous arsenic hydride was swept into an argon-diluted, air-entrained hydrogen flame of an atomic absorption spectrophotometer.

1.d Se and Sb in Coal

A ground and weighed coal (1.0 gram) was mixed with 1.5 to 2.0 grams of Eschka mixture (2 parts by weight of light calcined magnesium oxide to one part of anhydrous sodium carbonate) in a porcelain crucible. This mixture was covered with an additional 1.5 grams of Eschka mixture. The crucible was placed in a cold muffle furnace and heated to 500°C for one hour; the temperature was then increased to 750°C for 2-1/2 hours. It was necessary to maintain oxidizing conditions while ashing; therefore, air was forced at one litre/minute through a 1/4-inch stainless steel tubing located in the front of the furnace. Selenium was totally lost from coal in the absence of oxidizing conditions. Exhausted gases passed through a 1/4-inch stainless steel tube in the back of the furnace.[6] The crucible was cooled and the contents stirred with a platinum rod. If any unburned coal remained, the crucible was returned to the furnace and heated until all coal was ashed. The ash was transferred to a 150-ml beaker which contained 20 ml hot deionized water and 3 grams of tartaric acid. The crucible was rinsed carefully with 5 ml of concentrated reagent grade HCl and mixed with the contents in the beaker.

Two additional 5-ml aliquots of concentrated HCl were added to the mixture which was stirred after each addition. If any ash remained, additional acid was added to bring all material into solution. The solution was then diluted with deionized water to a final volume of 100 ml. This solution was used to determine the concentrations of Se and Sb.[4]

For Se, an aliquot of this solution was mixed with an equal amount of concentrated reagent grade HCl and placed in a water bath for at least 20 minutes to reduce Se^{6+} to Se^{4+}. The selenium was converted to the hydride by adding $SnCl_2$.[10] The gaseous selenium hydride was swept into an argon-diluted, air-entrained hydrogen flame of an atomic absorption spectrophotometer.[4]

For Sb, a 15-ml aliquot of the final solution was added to 5 ml of reagent grade concentrated HCl. KI and $SnCl_2$ were added to the solution and set aside for 20 minutes. Sodium borohydride was added to convert antimony to the hydride.[9] The gaseous antimony hydride was swept into an argon-diluted, air-entrained hydrogen flame of an atomic absorption spectrophotometer.[4,9]

1.e Cl in Coal

A ground and weighed coal sample (1.0 gram) was mixed with three grams of Eschka mixture in a procelain crucible. This mixture was covered with an additional two grams of Eschka mixture. The crucible was placed in a cold muffle furnace and gradually heated to 675 ± 25°C within one hour and was maintained at this temperature for an hour thereafter. The mixture was stirred with a platinum rod; and if any unburned coal remained, the crucible was returned to the furnace and heated until all coal was ashed. The ash was dissolved in 50 percent (V/V) nitric acid and the chloride was determined by potentiometric titration with a standard solution of silver nitrate.[7]

1.f F in Coal

A ground coal sample (0.1 g) was weighed into a 50-ml nickel crucible. Two grams of NaOH (three milliliters of a 0.67 g/ml NaOH solution) were added and oven-dried for 3-1/2 hours at 150°C. The crucible was placed in a muffle furnace at 300°C, heated to 600°C, and ashed for three hours. The ash was dissolved in a small amount of deionized water and transferred to a distillation flask containing silver perchlorate solution. After rinsing the crucible and adding the rinse solution to the flask, the fluoride was isolated by steam distillation and determined by the selective ion electrode.[8]

1.g Hg in Coal

A ground and weighed coal sample (0.2 g) was placed in a glass bottle. Five milliliters of deionized water and 5 ml of aqua regia (three volumes of concentrated reagent grade HCl to one volume of concentrated reagent grade HNO_3) were added, and the solution was heated two minutes in a water bath at 95°C. After the solution was cooled, 50 ml of deionized water and 15 ml $KMnO_4$ were added.

The solution was heated over a water bath for 30 minutes at 95°C and then cooled to room temperature. Six milliliters of sodium chloride-hydro-xylamine sulfate were added to reduce excess permanganate. Fifty-five milliliters of deionized water and 5 ml of stannous sulfate were added to the solution. The mercury was determined by cold vapor atomic absorption.[4]

2. Analysis Procedures for Particulate and Impinger Water from Train 1 Inlet to ESP

The particulate collected by the train 1 inlet was impinged on 90 mm spectrograde glass fiber filters. The filters were packaged in jars and sealed with plastic lids. A 250-ml Pyrex beaker covered with wax paper contained the free, dry fine particulate ash sample trapped by the cyclone (dry catch). Also a moist, charcoal-like particulate sample was collected by scrubbing the probe with acetone (probe rinse) that was packaged separately in a 250-ml Pyrex beaker covered with wax paper. The impinger water was stored in a glass sample bottle. Figure B-2 represents the analytical procedures for train 1 particulate and impinger water.

The filter was removed from the jar with platinum-tipped forceps. As much particulate matter as possible was knocked off with a platinum rod and composited with the dry catch in a tarred plastic cup. The weight of the particulate was determined by the difference--sufficient (>4 grams) for ordinary macrochemical analysis.

2.a Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, V, and Zn in Particulate

About 50 mg of sample were weighed accurately into a 1-ml platinum crucible, and 0.5-ml Ultrex HF and 0.05-ml Ultrex $HClO_4$ was added. The mixture was heated to dryness at a temperature below 250°C. The evaporation was repeated two more times with new portions of the acids. The residue was cooled and moistened with 0.05 ml Ultrex HCl and 0.5 ml deionized water. The mixture was covered and heated, without boiling, in a

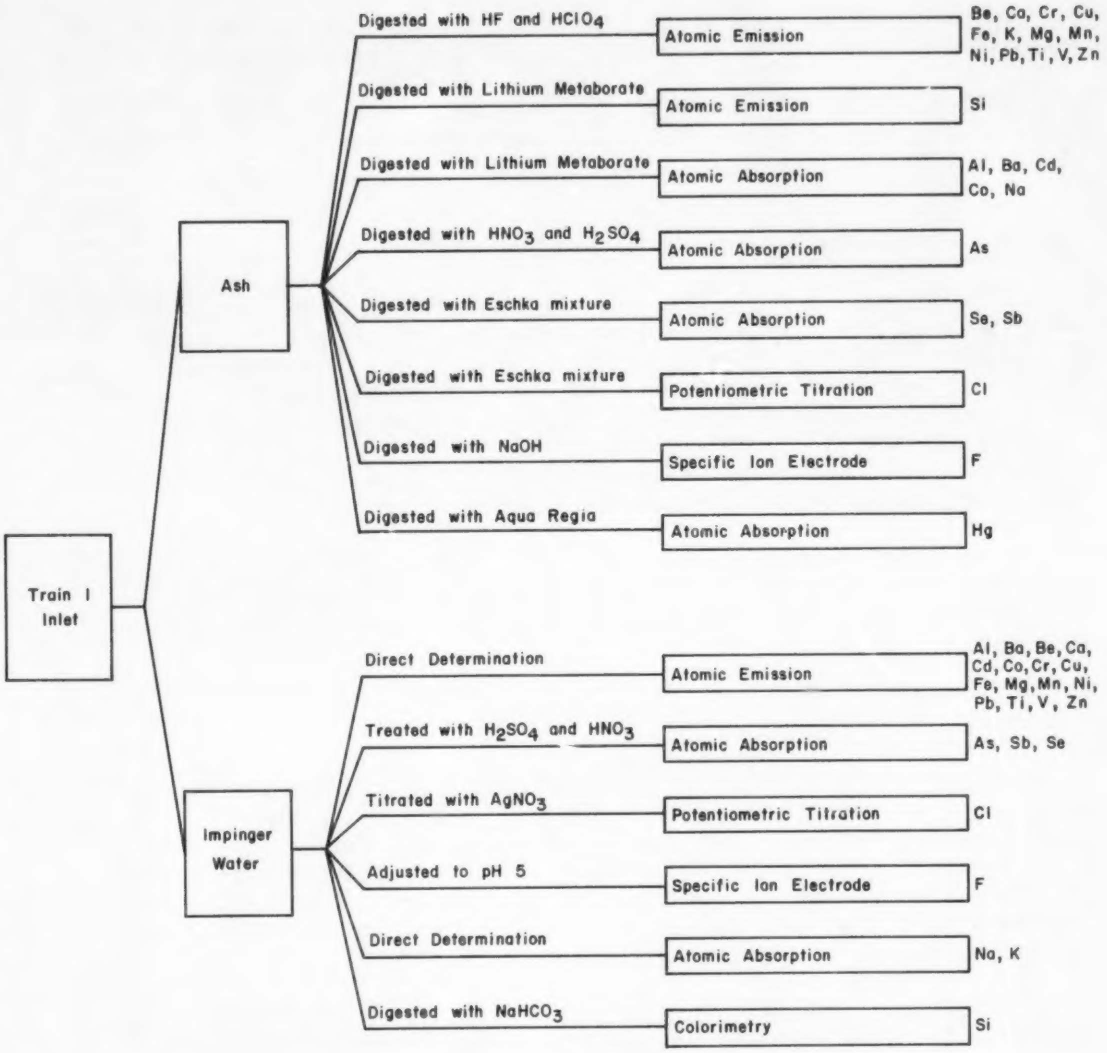

Train I Inlet
Ash
Digested with HF and $HClO_4$
Atomic Emission
Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, V, Zn
Digested with Lithium Metaborate
Atomic Emission
Si
Digested with Lithium Metaborate
Atomic Absorption
Al, Ba, Cd, Co, Na
Digested with HNO_3 and H_2SO_4
Atomic Absorption
As
Digested with Eschka mixture
Atomic Absorption
Se, Sb
Digested with Eschka mixture
Potentiometric Titration
Cl
Digested with NaOH
Specific Ion Electrode
F
Digested with Aqua Regia
Atomic Absorption
Hg
Impinger Water
Direct Determination
Atomic Emission
Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn
Treated with H_2SO_4 and HNO_3
Atomic Absorption
As, Sb, Se
Titrated with $AgNO_3$
Potentiometric Titration
Cl
Adjusted to pH 5
Specific Ion Electrode
F
Direct Determination
Atomic Absorption
Na, K
Digested with $NaHCO_3$
Colorimetry
Si

Figure B-2. Analytical procedures for trace element analysis of train I inlet to ESP.

sand bath until all salts and particulate matter were brought into solution. The cooled solution was transferred to a volumetric flask and made up to a final volume of 5.0 ml with 5 percent Ultrex HCl.

A 1.5-2.0-ml aliquot of this solution was used to determine the concentration of Be, Cr, Cu, K, V, Zn, Ni, and Pb by atomic emission.[1]

A 50 μl (0.05-ml) aliquot of the solution was diluted to 1.05 ml (21X) with 5 percent Ultrex HCl and used to determine the concentration of Ca, Fe, Mg, Mn, and Ti by atomic emission.[1]

2.b Al, Ba, Cd, Co, and Na in Particulate

An accurately weighed 0.5 g ground particulate sample was mixed with 2.0 g of reagent grade lithium metaborate in a platinum crucible and heated in a muffle furnace at 900°C until a clear melt was obtained. The mixture was cooled and placed in a beaker containing 8 ml of reagent grade HNO_3 and 150 ml of deionized water. The mixture was stirred vigorously until all material dissolved; tartaric acid was then added at a concentration of one percent. The solution was made up to a final volume of 250 ml with deionized water in a volumetric flask.[5]

An aliquot of this solution was used to determine the concentration of Si by atomic emission.[1] A second aliquot of this solution was used to determine the concentration of Al, Ba, Cd, Co, and Na by atomic absorption.[4]

2.c As in Particulate

An accurately weighed 0.5 g sample of ground particulate was placed in a flask, was mixed with 7.0 ml reagent (1 + 1) H_2SO_4 and 5.0 ml concentrated redistilled HNO_3, and was evaporated to SO_3 fumes. The mixture was cooled, 25.0 ml of deionized water was added, and the evaporation procedure was repeated to expel oxides of nitrogen. The mixture was diluted to 100.0 ml with deionized water, and the arsenic was converted to the hydride by adding reducing reagents.[12]

The gaseous arsenic hydride was swept into an argon-diluted, air-entrained hydrogen flame of an atomic absorption spectrophotometer.[12,4]

2.d Se and Sb in Particulate

An accurately weighed ground particulate sample (about 0.6 g) was mixed with 1.5 to 2.0 g of Eschka mixture in a porcelain crucible. This mixture was covered with an additional 1.5 g of Eschka mixture. The crucible was placed in a cold muffle furnace and heated to 500°C for one hour; the temperature was then increased to 750°C for 2-1/2 hours. It was necessary to maintain oxidizing conditions while ashing; therefore, air was forced at one litre/minute through a 1/4-inch stainless steel tubing located in front of the furnace. Selenium is partially lost from ash in the absence of oxidizing conditions. Exhausted gases passed through a 1/4-inch stainless steel tubing in the rear of the furnace.[6] The crucible was cooled and the contents were stirred with a platinum rod.

The mixture was transferred to a 150-ml beaker which contained 20 ml of hot deionized water and three grams of tartaric acid. The crucible was rinsed carefully with 5 ml of concentrated reagent grade HCl and mixed with the contents in the beaker.

Two additional 5-ml aliquots of concentrated HCl were added to the mixture which was stirred after each addition. If any particulate remained, additional acid was added to bring all material into solution. The solution was then diluted to a final volume of 100 ml with dionized water. This solution was used for the determination of Se and Sb.[4]

For Se, an aliquot of this solution was mixed with an equal amount of concentrated reagent grade HCl and placed in a water bath for at least 20 minutes to reduce Se^{6+} to Se^{4+}. The selenium was converted to the hydride by adding $SnCl_2$.[4] The gaseous selenium hydride was swept into an argon-diluted hydrogen flame of an atomic absorption spectrophotometer.[6]

For Sb, a 15-ml aliquot of the final solution was added to 5 ml of reagent grade concentrated HCl. Two milliliters of 20 percent KI were added to the solution and set aside for 20 minutes. $SnCl_2$ was added to convert antimony to the hydride.[10] The gaseous antimony hydride was swept into an argon-diluted hydrogen flame of an atomic absorption spectrophotometer.[6]

2.e Cl in Particulate

A 1.0 g ground particulate sample was mixed with 1.5-2.0 g of Eschka mixture in a porcelain crucible. This mixture was covered with an additional 1.5 g of Eschka. The crucible was placed in a cold muffle furnace and heated to 500°C for 1 hour, and then the temperature was increased to 750°C for 2-1/2 hours.

The particulate was transferred to a 150-ml beaker which contained 20 ml of hot deionized water. Forty milliliters of reagent grade HNO_3 (1 + 1) were then added. The beaker was covered with a watch glass and the contents stirred occasionally with a platinum rod to expedite solution.

An aliquot of this solution was titrated with 0.25N $AgNO_3$. Silver and silver-silver chloride electrodes were used, and the endpoint was determined by a potentiometer.[7]

2.f F in Particulate

For the determination of F, a 1.0 g ground particulate sample was weighed into a 50-ml nickle crucible. Three milliliters of 2N NaOH solution were added and oven-dried for 3-1/2 hours at 150°C. The crucible was placed in a muffle furnace at 300°C and then heated to 600°C for 3 hours.

The particulate was dissolved in a small amount of deionized water and 4 to 5 drops of 30 percent H_2O_2 were added to oxidize sulfites to sulfates, and then boiled to destroy excess peroxide. Fluoride was isolated by steam distillation and the concentration was determined by the specific ion electrode method.[8]

2.g Hg in Particulate

To determine Hg, an 0.2 g ground particulate sample was placed in a glass bottle. Five milliliters of deionized water and 5 ml of aqua regia were added, and the solution was heated 2 minutes in a water bath at 95°C. The solution was cooled and 50 ml of deionized water and 15 ml $KMnO_4$ were added. The solution was heated over a water bath for 30 minutes at 95°C and then cooled to room temperature. Six milliliters of sodium chloride-hydroxylamine sulfate were added to reduce excess permanaganate. Fifty-five milliliters of deionized water and 5 ml of stannous sulfate were added; then the concentration of mercury was determined by atomic absoption.

2.h Al, Ba, Be, Ca, Cd, Cu, Cr, Fe, Mg, Mn, Ni, Pg, Ti, V, and Zn in Impinger Water

A 1.5-2.0-ml aliquot of the impinger water sample was used for the direct determination of Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn.[1]

2.i As in Impinger Water

For the determination of As, a 25.0-ml aliquot was mixed with 7.0 ml reagent grade (1 + 1) H_2SO_4 and 5.0 ml of concentrated redistilled HNO_3, and was evaporated to SO_3 fumes. The mixture was cooled, and 25.0 ml of deionized water were added; the evaporation procedure was repeated to expel oxides of nitrogen.[11] The mixture was diluted to 100.0 ml with deionized water and the arsenic was converted to the hydride by adding $SnCl_2$.[10] The gaseous arsenic hydride was swept into an argon-diluted hydrogen flame of an atomic absorption spectrophetometer.[4,12]

2.j Cl in Impinger Water

For Cl a 25.0-ml aliquot was pipetted into a 250-ml beaker. After acidifying with sulfuric acid, the solution was boiled with peroxide to destroy sulfite. After boiling in basic media to remove peroxide, the solution was acidified with nitric acid and potentiometrically titrated with standard silver nitrate.[11]

2.k F in Impinger Water

A 25.0-ml aliquot was mixed with 25.0 ml of buffer (pH 5.0-5.5) in a Pyrex beaker. The concentration of fluoride was determined potentiometrically using a selective ion fluroide electrode.[4]

2.1 Se and Sb in Impinger Water

These elements were determined after digestion by gaseous hydride generation with an tomic absorption analytical finish.[9,10]

2.m Si in Impinger Water

The silica was determined by the automated molybdosilicate method.[11] Automation by Technicon Autoanalyzer improved the detection limit from 1 to 0.1 mg/l.

3. Analytical Procedures for Particulate and Impinger Water from Train 1 Outlet to ESP

Figure B-3 represents the analytical procedures used for Train 1 outlet particulate and impinger water.

The fine particulate collected by the Train 1 outlet was impinged on 90 mm spectrograde glass fiber filters. The filters were packaged in glass jars having plastic caps, [unlike the inlet, a separate free, dry ash (dry catch) sample was absent]; but there was a moist, charcoal-like particulate sample, collected by scrubbing the probe with acetone (probe rinse) that was packaged separately in a 250-ml Pyrex beaker that was sealed with wax paper. Because of the extremely small sample size, sufficient particulate for chemical analysis could not be mechanically dislodged from the filter or scraped from the beaker. Therefore, the particulate was extracted with absolute ethanol by sonifying the material on the filter and in the beaker. Because of the high background of these substrates, it was thought the concentration of Na and Si were not valid; so these results were not reported.

One-fourth of the filter was reserved for the analysis of chloride and flouride. The glass filter was placed on a sheet of Teflon, and a Teflon wedge one-fourth the size of the filter was used as a guide in cutting a one-quarter section of the filter A surgical grade steel scapel was used to cut the filter. Any particulate sticking to the Telfon wedge was brushed onto the quartered filter with a camel hair brush. The one-quarter section of the filter was used to determine F and Cl in the particulate. The remaining three-quarter filter section was used for the determination of Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Na, Mg, Mn, Ni, Pb, Sb, Se, Ti, V, and Zn in particulate.

The probe rinse material received in the 250-ml Pyrex beaker was extracted by sonification with a sufficient amount of absolute ethanol to cover all the particulate matter. This rinse material was transferred quantitatively with additional ethanol to a tarred 100-ml Teflon beaker. The Teflon beaker was dried under an infrared lamp for 10 minutes and desiccated for 30 minutes over silica gel before it was tarred.

The three-fourth filter portion was dried on aluminum foil under an infrared lamp for 10 minutes and desiccated over silica gel for 30 minutes. The tar weight was measured to the nearest one-hundredth of a milligram.

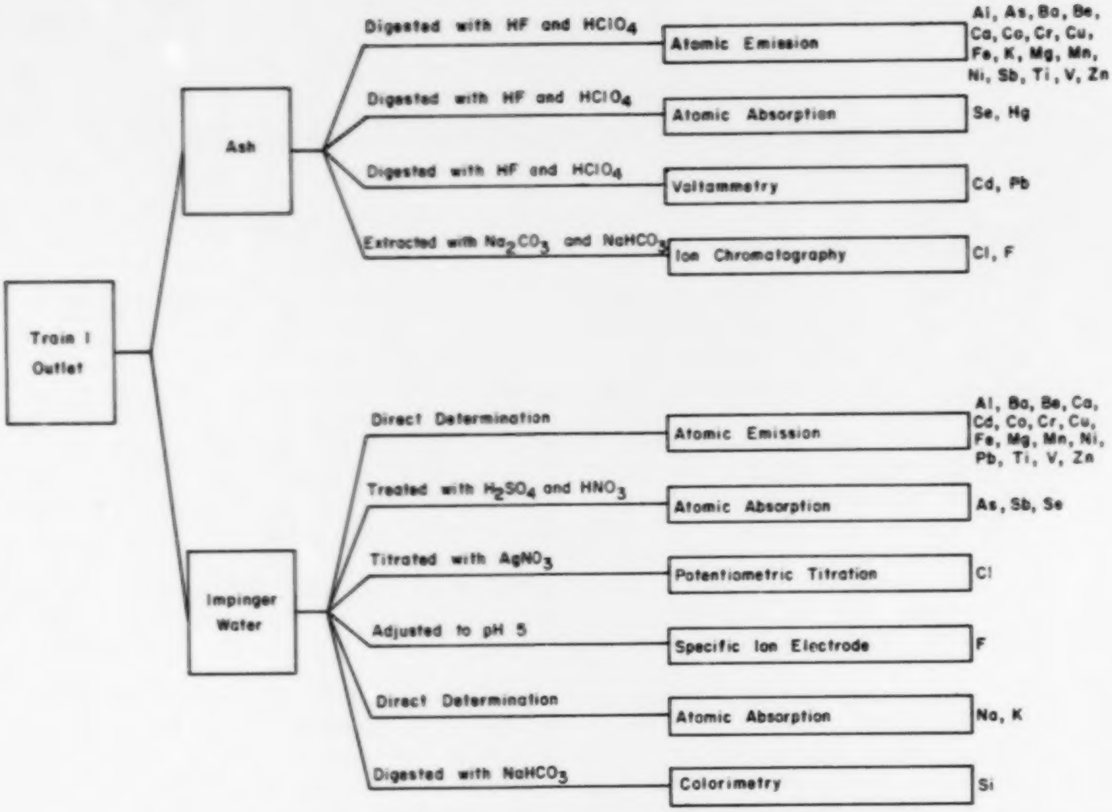

Train I Outlet
Ash
Digested with HF and HClO4
Atomic Emission
Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Sb, Ti, V, Zn
Digested with HF and HClO4
Atomic Absorption
Se, Hg
Digested with HF and HClO4
Voltammetry
Cd, Pb
Extracted with Na2CO3 and NaHCO3
Ion Chromatography
Cl, F
Impinger Water
Direct Determination
Atomic Emission
Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn
Treated with H2SO4 and HNO3
Atomic Absorption
As, Sb, Se
Titrated with AgNO3
Potentiometric Titration
Cl
Adjusted to pH 5
Specific Ion Electrode
F
Direct Determination
Atomic Absorption
Na, K
Digested with NaHCO3
Colorimetry
Si

Figure B-3. Analytical procedures for trace element analysis of train I outlet from ESP.

The filter was removed from the foil with platinum-tipped forceps and placed in the 100-ml Teflon beaker containing the ethanol slurry from the probe rinse. Additional ethanol was added to cover the filter. The particulate was removed from the filter by placing the beaker briefly in an ultrasonic bath. The extracted filter was removed from the beaker with platinum-tipped forceps, returned to the aluminim foil, and saved for possible future examination. The ethanol was evaporated without boiling and dried an additional 10 minutes under an infrared lamp. After desiccation over silica gel for 30 minutes, the residue in the Teflon beaker was reweighed and the weight extracted from three-fourths of the filter; probe rinse material was determined by difference. The Teflon beaker containing this combined residue was stored over silica gel for chemical analysis of 22 elements (Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Na, Mg, Mn, Ni, Pb, Sb, Se, Ti, V, and Zn).[2]

Each composited particulate residue (see Table B-2) was digested with 5 ml Ultrex HF and one drop (0.05 ml) of Ultrex $HClO_4$. The mixture was evaporated slowly, without boiling, to dryness in a sand bath at a temperature not exceeding 220°C. The evaporation was repeated a second time with 3 ml of Ultrex HF and one drop Ultrex $HClO_4$, and a third time with 1 ml of Ultrex HF and one drop Ultrex $HClO_4$. The salts formed by this triple evaporation were dissolved and diluted according to sample weight.

Referring to Table B-2, the salts formed by the triple evaporation for the blank (0.49 mg), test 8 (113.57 mg), and test 4 (136.29 mg) were mixed separately with 0.25 ml of concentrated hydrochloric acid (Baker Ultrex reagent). After allowing a few minutes for dissolution, the mixture was diluted with 2.5 ml of reagent water. The solution was covered with a watch glass and heated just below boiling for about five minutes or longer, as necessary, to dissolve the salts and large particulate clumps. When the solution had cooled, the watch glass and beaker were washed with 1 ml of 5 percent (V/V) Ultrex hydrochloric acid; and the solution was poured through a plastic funnel into a 5.0-ml volumetric flask. After rinsing the beaker dropwise with an additional 10 drops (0.5 ml) of 5 percent (V/V) Ultrex hydrochloric acid and combining this rinsing solution with the solution in the volumetric flask, the solution was diluted to exactly 5 ml with five percent (V/V) Ultrex hydrochloric acid. Immediately the solution was poured into a 10-ml Teflon test tube and capped with a Nalgene No. 16 polyethylene closure.

The salts formed by evaporation with hydrofluoric acid for tests 7 (149.24 mg), 9 (159.86 mg), and 1 (235.96 mg) were mixed separately with 0.5 ml Ultrex HCl for partial dissolution and then 5.0 ml deionized water with heating to dissolve the remaining particulate. After cooling to room temperature, the solutions were transferred to separate 10.0-ml volumetric flasks. The beakers were rinsed with 10 drops (0.5 ml) of 5 percent (V/V) Ultrex HCl and added to the solution in the flasks. The solutions were diluted to 10.0 ml with 5 percent (V/V) Ultrex HCl and stored in capped Teflon test tubes for chemcial analysis.

The salt residues for tests 5 (289.54 mg), 3 (443.11 mg), and 2 (618.88) were treated separately with 1.25 ml Ultrex HCl and 12.5 ml deionized water and heated until all salts and particulate matter had

TABLE B-2. EXTRACTED WEIGHTS OF TRAIN 1 OUTLET PARTICULATE[1]

Test No.	Lab Extracted Weight (mg)
1	235.96
2	618.88
3	443.11
4	136.29
5	289.54
6	1403.72
7	149.24
8	113.57
9	159.86
Blank	0.49[2]

---

[1] Weight recovered by extracting and compositing three-fourths of the material on the filter with all the probe material.

[2] Weight determined by extracting three-fourths of the blank filter received with the samples.

dissolved. After cooling to room temperature, the solutions were transferred to separate 10.0-ml volumetric flasks. The beakers were rinsed with 10 drops (0.5 ml) of 5 percent (V/V) Ultrex HCl and added to the solution in flasks. The solutions were diluted to 25.0 ml with 5 percent (V/V) Ultrex HCl and stored in Teflon bottles for chemical analysis.

The residue for test 6 (1403.72 mg) was mixed with 2.5 ml Ultrex HCl and 25.0 ml deionized water and heated until all salts and particulate matter had dissolved. After cooling to room temperature, the solution was transferred to a 50.0-ml volumetric flask. The beaker was rinsed with 10 drops (0.5 ml) of 5 percent (V/V) Ultrex HCl and added to the solution in the flask. The solution was then diluted with 5 percent (V/V) Ultrex HCl to a final volume of 50.0 ml and stored in a Teflon bottle for chemical analysis.

3.a Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Ni, Pb, Sb, Se, Ti, V, and Zn in Particulate

A 1.5-2.0-ml aliquot of each of the diluted solutions was used to determine the concentration of Ba, Be, Cu, K, Ti, V, Zn, Co, As, Sb, Al, Ca, Cr, Fe, Mg, Mn, and Ni by atomic emission.[1] A 1-ml aliquot was used for the atomic absorption determination of Hg by the micro-cold vapor technique.[3] A 0.5-ml aliquot was used for the atomic absorption determination of Se by micro-gaseous hydride technique.[3,4] A 1-ml aliquot was treated with 2.0 ml of redistrilled HNO_3, and the concentrations of Cd and Pb were determined by differential pulse anodic stripping voltammetry.[13]

3.b Cl and F in Particulate

The one-fourth section of the glass fiber filter containing the particulate was folded and placed in a 15-ml graduated centrifuge tube. This section of the filter was treated with 4.0 ml of a solution containing 0.0024 M Na_2CO_3 and 0.003 M $NaHCO_3$. The centrifuge tube was sealed with aluminum foil and sonified in a water bath and heated for an hour to extract the soluble chloride and fluoride. The solution was cooled, and a 250-µl aliquot was used for the determination of Cl and F by ion chromatography.[14] The results for fluoride are for the free portion only because the fluorosilicates were probably not extracted. Calculations for concentration in µg/g are based on weights determined in the field (see Table B-3).

TABLE B-3. EXTRACTED WEIGHT OF TRAIN 1 OUTLET PARTICULATE FOR Cl AND F[1]

Test No.	Field Weight (mg)
1	36.14
2	34.85
3	35.49
4	10.62
5	35.22
6	37.74
7	21.81
8	19.38
9	26.14

---

[1] One-fourth of a filter was used for Cl and F chemical analysis.

3.c Impinger Water

The train 1 outlet impinger water was analyzed according to the same procedures as the train 1 inlet.

4. Analytical Procedures for Vapor Phase Trace Elements from Train 2

The reagents used for the collection of vaporous trace elements were K_2CO_3, KOH, H_2O_2, and H_2SO_4. The K_2CO_3 reagent matrix was 10 percent (W/V) K_2CO_3 in water; the KOH reagent matrix was 1 M KOH in water; the H_2O_2 reagent matrix was a mixture of 3 percent (1.8 M) H_2O_2, 0.14 M HNO_3, and 0.02 M $AgNO_3$ in water; the H_2SO_4 reagent matrix was concentrated sulfuric acid. All reagents except K_2CO_3 were reagent grade. The K_2CO_3 was Ultrex grade from Baker Chemical Co. The anlytical procedures depicted in Figure B-4 were used for the analysis of trace elements. As shown, the K_2CO_3 and HOH samples were analyzed by the same procedures.

4.a Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn in the K_2CO_3 and KOH Matrix

For the K_2CO_3 and KOH samples, a 5.0-ml aliquot was placed in a 100-ml volumetric flask and acidified with 1.0 ml redistilled HNO_3. The sample was diluted with deionized water to a final volume of 100.0 ml. A 1.5-2.0-ml aliquot of the final solution was used to determine the concentration of Al, Ba, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn by atomic emission.[1]

4.b As and Sb in K_2CO_3 and KOH Matrix

A 15-ml aliquot of the sample was transferred to a 50-ml volumetric flask. The sample was treated with 2.0 ml concentrated reagent grade HCl and diluted to a final volume of 50.0 ml with deionized water. As and Sb were determined without digestion by gaseous hydride generation with an atomic absorption analytical finish.[9,12]

4.c Cl and F in K_2CO_3 and KOH Matrix

For Cl a 25-ml aliquot was acidified with H_2SO_4 and digested; the Cl was determined by potentiometric titration with standard silver nitrate.[11] (Refer to section 2.j Cl in Impinger Water.) For F, a 25-ml aliquot was acidified and the fluoride was determined by selective ion electrode.[4] (Refer to section 2.k F in Impinger Water.)

4.d Se in K_2CO_3 and KOH Matrix

For Se, concentrated reagent grade HNO_3 was added to 30.0 ml to achieve a pH<2. The sample was treated with 5 percent KMO_4 to maintain a purple tint for at least 30 minutes. An equal volume of concentrated reagent grade HCl was added, and the sample was digested in a steam bath

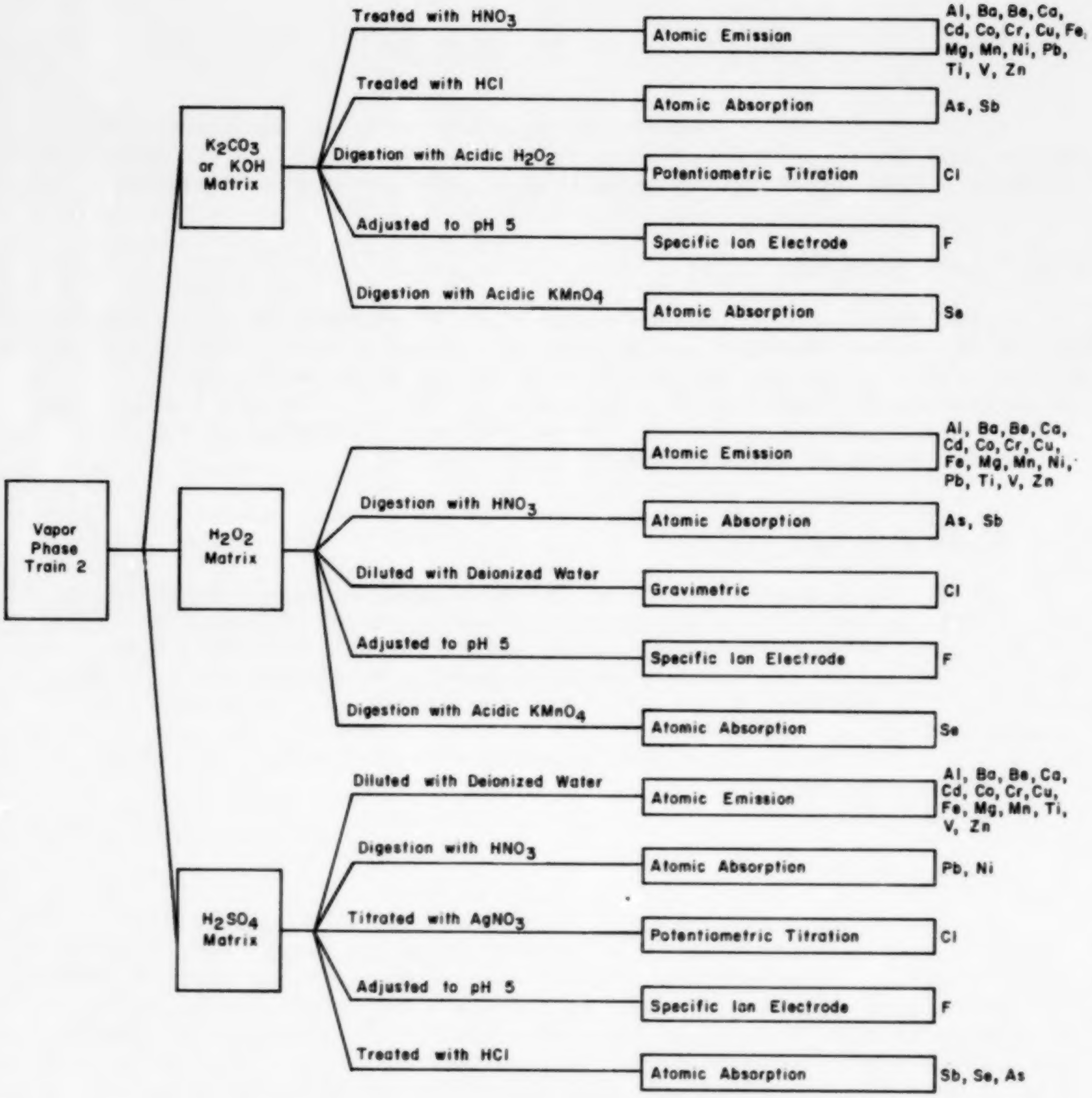

Vapor Phase Train 2
K$_2$CO$_3$ or KOH Matrix
Treated with HNO$_3$
Atomic Emission
Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn
Treated with HCl
Atomic Absorption
As, Sb
Digestion with Acidic H$_2$O$_2$
Potentiometric Titration
Cl
Adjusted to pH 5
Specific Ion Electrode
F
Digestion with Acidic KMnO$_4$
Atomic Absorption
Se
H$_2$O$_2$ Matrix
Atomic Emission
Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, Zn
Digestion with HNO$_3$
Atomic Absorption
As, Sb
Diluted with Deionized Water
Gravimetric
Cl
Adjusted to pH 5
Specific Ion Electrode
F
Digestion with Acidic KMnO$_4$
Atomic Absorption
Se
H$_2$SO$_4$ Matrix
Diluted with Deionized Water
Atomic Emission
Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ti, V, Zn
Digestion with HNO$_3$
Atomic Absorption
Pb, Ni
Titrated with AgNO$_3$
Potentiometric Titration
Cl
Adjusted to pH 5
Specific Ion Electrode
F
Treated with HCl
Atomic Absorption
Sb, Se, As

Figure B-4. Analytical procedures for vaporous trace elements analysis of train 2 at 95°C for at least 20 minutes. The sample was cooled and diluted with 6 M HCl to a known volume and analyzed for selenium by atomic absorption using the gaseous hydride technique.[10]

4.e Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn in H_2O_2 Matrix

A 1.5-2.0-ml aliquot was used to determine the concentration of Al, Ba, Be, Cu, Cd, Co, Cr, Ca, Fe, Mg, Mn, Ni, Pb, Ti, V, and Zn by atomic emission.w The concentrations were also verified by atomic absorption.[4]

4.f As and Sb in H_2O_2 Matrix

A 20.0-ml aliquot of the H_2O_2 matrix was digested to SO_3 fumes with 5.0 ml of concentrated redistilled HNO_3 and 5.0 ml reagent grade (1 + 1) H_2SO_4. The solution was cooled and 10 ml of distilled water and 10 ml of concentrated redistilled HNO_3 were added. The solution was fumed again, and the concentration of arsenic and antimony was determined by atomic absorption using the gaseous hydride technique.[9,12]

4.g Cl and F in H_2O_2 Matrix

For the determination of Cl, a 10.0-ml aliquot of the H_2O_2 matrix was diluted to 100 ml with deionized water and filtered through a preweighed glass fiber filter. The filter was rinsed with deionized water, dried at 110°C, and reweighed. The difference in weight was the chlorine capture.[15] To determine F, an aliquot of the H_2O_2 matrix was mixed with an equal volume of buffer (pH 5.0-5.5) in a Pyrex beaker. The concentration of fluoride was determined potentiometrically using a selective ion fluoride electrode.[4]

4.h Se in H_2O_2 Matrix

For the determination of Se, a 30.0-ml aliquot of H_2O_2 matrix was treated with a sufficient amount of reagent grade 5 percent $KMnO_4$ (about 7 ml) to maintain a purple tint for at least 30 minutes. An equal volume of concentrated reagent grade HCl was added and the sample was digested in a steam bath at 95°C for at least 20 minutes. The solution was cooled and diluted with 6 M HCl to 100 ml in a volumetric flask. The concentration of selenium was determined by atomic absorption using the gaseous hydride technique.[10]

4.i Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ti, V, and Zn in H_2SO_4 Matrix

For the H_2SO_4 samples, a 5.0-ml aliquot was transferred to a volumetric flask and diluted to 100.0 ml with deionized water. A 1.5-20.0-ml aliquot was used to determine the concentration of Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ti, V, and Zn by atomic emission.[1]

4.j Pb and Ni in H_2SO_4 Matrix

A 5.0-ml aliquot of the H_2SO_4 matrix was transferred to a volumetric flask, diluted to 100.0 ml with deionized water, and filtered through a Gelman 0.45 µm membrane filter. The filter containing the insoluble material was transferred to a 250-ml beaker and 3.0 ml of concentrated redistilled HNO_3 was added. The beaker was covered with a watch glass and heated gently to dissolve the filter. The temperature was increased to digest the material and to evaporate the acid. The mixture was cooled and 3.0 ml of concentrated redistilled HNO_3 were added. The beaker was covered and heated until the digestion was completed. A 2.0-ml aliquot of redistilled (1 + 1) HCl was added and the residue heated gently to dissolve the material. A small portion of deionized water was used to wash down the sides of the beaker. The mixture was transferred to a volumetric flask and diluted with deionized water to a final volume of 25 ml. An aliquot of the final solution was used to determine the concentration of Pb and Ni by atomic absorption.[4]

4.k As in H_2SO_4 Matrix

A 15.0-ml aliquot of the H_2SO_4 matrix was pipetted into 15.0 ml of deionized water and then diluted to 50.0 ml with deionized water. The concentration of arsenic was determined by atomic absorption using the gaseous hydride technique.[12]

4.1 Cl and F in H_2SO_4 Matrix

An aliquot was diluted. The chloride and fluoride were determined according to sections 2.j and 2.k for these species in impinger water.

4.m Se and Sb in H_2SO_4 Matrix

For Sb, a 15.0-ml sample of the H_2SO_4 matrix was pipetted into a 50.0 ml volumetric and was diluted to 50.0 ml with deionized water. The concentration of antimony was determined by atomic absorption using the gaseous hydride technique.[9] For Se, a 5.0-ml sample was added to 25 ml of deionized water and 5 percent KMO_4 was added until a purple tint was maintained for 30 minutes. An equal volume of concentrated reagent grade HCl was added and the sample was digested in a steam bath at 95°C for at least 20 minutes. The sample was cooled and diluted with 6 M HCl to a known volume and analyzed for selenium by atomic absorption using the gaseous hydride technique.[10]

5. Analytical Procedures for Mercury from Train 4

The reagents used for the collection of mercury vapor were K_2CO_3 and $KMnO_4$, in HNO_3. There were three types of samples from the mercury train: K_2CO_3, $KMnO_4$ in HNO_3, and an oxalic acid rinse of the impingers that contained the $KMnO_4$ solution. The K_2CO_3 was 10 percent (W/V) K_2CO_3 in water; the $KMnO_4$ in HNO_3 was three percent (W/V) $KMnO_4$ in 14.2 percent

(V/V) HNO_3; the oxalic acid used for rinsing was 10 percent (W/V) oxalic acid. All reagents except K_2CO_3 were reagent grade. The K_2CO_3 was Ultrex grade from Baker Chemical Co. The analytical flow scheme is given by Figure B-5.

5.a Hg in K_2CO_3 Matrix

The mercury concentration in the K_2CO_3 matrix was determined by acidifying 100 ml of sample with 5.0 ml of concentrated reagent grade H_2SO_4. Thereafter, the solution was treated for mercury by the cold vapor atomic absorption technique beginning with section 8.1 on page 124 of footnoted reference.[4]

5.b Hg in $KMnO_4$ Matrix

A 10.0-ml sample of the $KMnO_4$ matrix was diluted with deionized water to 100.0 ml. Thereafter, the solution was treated for mercury by the cold vapor atomic absorption technique beginning with section 8.1 on page 124 of the footnoted reference.[4] Hydroxylamine was added until the permanganate color just dissipated.

5.c Hg in Oxalic Acid Rinse

A 75.0-ml sample of the oxalic acid rinse was diluted to 100.0 ml with deionized water. Five milliliters of concentrated reagent grade H_2So_4 and 2.5 ml concentrated redistilled HNO_3 were added. Hydroxylamine and stannous chloride were added to generate atomic mercury for determination by the cold vapor atomic absorption technique.[4] Calibration was achieved in oxalic acid having the same concentration as that employed for the diluted sample. Permanganate was not used to digest the sample because permanganate is consumed endlessly by the oxalic acid.

6. Analytical Procedures for Analysis of Fine Particulate from Brink Impactor

The fine particulate collected by the Brink Impactor was impinged on aluminum pans and stored in a polyethylene cup. Figure B-6 represents the analytical procedures used for trace element determination of the fine particulate.

In order to obtain sufficient sample weight for analysis, it was necessary to composit samples by tests and plates. Tables B-4 and B-5 represent the compositing scheme of the Brink Impactor samples.

6.a Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Ti, V, and Zn in Particulate

After removing the sample number from the polyethylene cup with a Kim-Wipe moistened with absolute ethanol, the cup and the aluminum pan

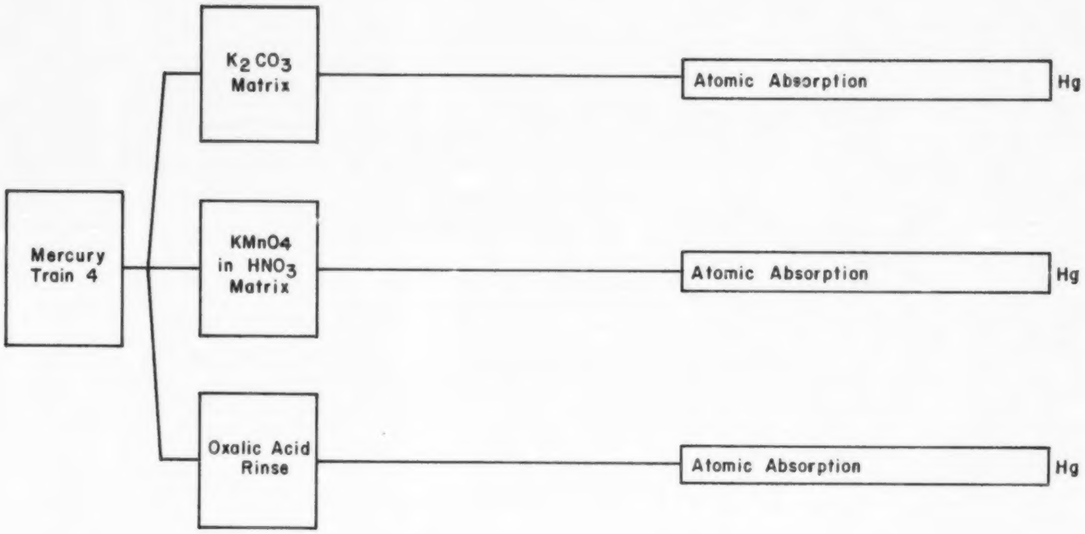

K_2CO_3 Matrix
Atomic Absorption
Hg
Mercury Train 4
$KMnO_4$ in HNO_3 Matrix
Atomic Absorption
Hg
Oxalic Acid Rinse
Atomic Absorption
Hg

Figure B-5. Analytical procedures for mercury from train 4

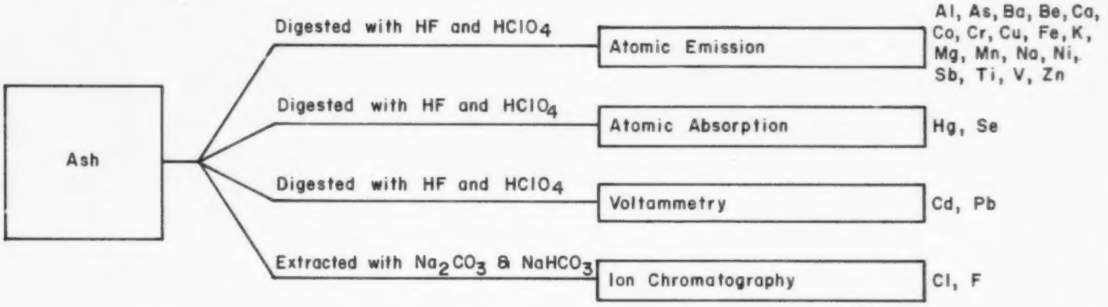

Ash
Digested with HF and HClO4
Atomic Emission
Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sb, Ti, V, Zn
Digested with HF and HClO4
Atomic Absorption
Hg, Se
Digested with HF and HClO4
Voltammetry
Cd, Pb
Extracted with Na2CO3 & NaHCO3
Ion Chromatography
Cl, F

Figure B-6. Analytical procedures for trace element analysis of Brink Impactor fine particulate

TABLE B-4. COMPOSITING SCHEME FOR BRINK IMPACTOR FINE PARTICULATE FOR DETERMINING 22 ELEMENTS

Composite of Field Tests	Composite of Plates	Approximate Particle Size (μm)	Extracted Weight (mg)
1+10+11	0c+1	>3	48.36
15+16+17	0c+1	>3	69.30
3+12	0c+1	>3	24.43
13+14	0c+1	>3	27.03
1+10+11+15+16+17	2+3	1-3	20.69
3+12+13+14	2+3	1-3	8.09
1+10+11+15+16+17	4+5	0-1	1.86
3+12+13+14	4+5	0-1	2.35
Blank	-	-	-

TABLE B-5. COMPOSITING SCHEME FOR BRINK IMPACTOR FINE PARTICULATE FOR DETERMINING Cl AND F

Composite of Field Tests	Composite of Plates	Approximate Particle Size (μm)	Extracted Weight (mg)
2	0c+1	>3	18.50
4	0c+1	>3	24.20
2	2+3	1-3	4.37
4	2+3	1-3	1.97
2	4+5	0-1	0.22
4	4+5	0-1	0.18
Blank	-	-	0.02

containing the fine particulate were dried for 10 minutes under an infrared lamp and desiccated for 30 minutes over silica gel. The tar weight was measured to the nearest one-hundredth of a milligram. The aluminum pan was placed in a 100-ml Teflon beaker with platinum-tipped forceps, and any particulate matter remaining in the polyethylene cup was removed with absolute ethanol and poured into the beakers. Additional ethanol was added to the beaker to cover the aluminum pan.

The particulate matter was removed from the aluminum pan by briefly placing the beaker in an ultrasonic bath. The pan was removed from the beaker with platinum-tipped forceps and returned to the polyethylene cup to be dried under an infrared lamp for 10 minutes. After desiccation over silica gel for 30 minutes, the pan and cup were reweighed. The weight extracted was determined by difference.

The next sample to be composited was extracted, dried, and weighed as in the above procedure. This sample was combined with the material in the beaker from the previous sample, and the added weight was determined by difference between empty and full sample vessels. This process was repeated for each sample to yield the composited samples listed in Table B-4. After compositing the samples, the ethanol was evaporated to dryness under an infrared lamp and the beaker was stored in a desiccator. The extraction and compositing scheme is similar to that used by Accu-Labs.[16]

The composited fine particulate (2-50 mg) in the 100-ml Teflon beaker was treated with 1.5 ml of Ultrex HF and one drop (0.05 ml) of Ultrex $HClO_4$. The mixture was evaporated slowly, without boiling, to dryness in a sand bath at a temperature not exceeding 220°C. The evaporation was repeated twice with 1.0 ml Ultrex HF and one drop (0.05 ml) Ultrex $HClO_4$. The residue was cooled and moistened with 0.25 ml Ultrex HCl. After a few minutes allowed for dissolution, the mixture was diluted with 2.5 ml of deionized water, covered with a watch glass, and heated just below boiling until all salts and particulate matter had dissolved. When the solution had cooled, the watch glass and beaker were washed with 1 ml of 5 percent (V/V) Ultrex HCl and combined with the solution in the volumetric flask. The solution was diluted to 5.0 ml with 5 percent (V/V) Ultrex HCl, poured into a 10-ml Teflon test tube, and capped with a polyethylene closure.[2]

A 1.5-2.0-ml aliquot of the solution was used to determine the concentration of Ba, Be, Cu, K, V, Ti, Zn, Al, Ca, Cr, Fe, Mg, Mn, Ni, Co, As, Sb, and Na by atomic emission.[1] Another aliquot was used to determine the concentration of Hg[3] and Se[10] by atomic absorption with cold vapor and hydride generation, respectively. A microvapor vessel and microcell were used for generating the atomic mercury in a 1-ml aliquot, and the microvapor vessel was used to form gaseous selenium hydride in a 0.5-ml aliquot.[3] A 1-ml aliquot of the solution was treated with 2.0 ml of redistilled HNO_3, and the Cd and Pb were determined by differential pulse anodic stripping voltammetry beginning with section 8.4 in the footnoted reference.[13]

The extraction and digestion procedures, repeated for an unexposed aluminum pan, served as a blank for the chemical analysis.

6.b Cl and F in Particulate

Two tests were reserved for the determination of Cl and F. Because of small sample size, it was necessary to composite by plates. Table B-5 shows the compositing scheme used for the fine particulate.

The fine particulate impinged on the aluminum pan in the polyethylene cup (after removing the sample number from the cup with a Kim-Wipe moistened with absolute ethanol) was dried for 10 minutes under an infrared lamp and desiccated for 30 minutes over silica gel. The tar weight was measured to the nearest one-hundredth of a milligram. The aluminum pan was placed in a 30-ml Pyrex beaker with platinum-tipped forceps, and any particulate matter remaining in the polyethylene cup was removed with absolute ethanol and poured into the beaker. Additional ethanol was added to the beaker to cover the aluminum pan.

The particulate matter was removed from the aluminum pan by briefly placing the beaker in an ultrasonic bath. The pan was removed from the beaker with platinum-tipped forceps and returned to the polyethylene cup to be dried under an infrared lamp for 10 minutes. After desiccation over silica gel for 30 minutes, the pan and cup were reweighed. The weight extracted was determined by difference.

The next sample to be composited was extracted, dried, and weighed as in the above procedure. This sample was combined with the material in the beaker from the previous sample and the added weight was determined by difference between empty and full sample vessels. This process was repeated for each sample to yield the composited samples listed in Table B-4. After compositing the samples, the ethanol was evaporated to dryness under an infrared lamp and the beaker was stored in a desiccator.[16]

Depending on sample size (0.1-30 mg), 1-4 ml of a solution containing 0.0024 M Na_2CO_3 and 0.003 M $NaHCO_3$ was pipetted into the beaker containing the composited sample. This mixture was covered with aluminum foil and sonified in a water bath for an hour and heated to extract the soluble fluoride and chloride. The supernatant was decanted and centrifuged; and about a 0.3-ml aliquot was withdrawn for determination of Cl and F by ion chromatography.[14] The results for fluoride are for the free portion only because the fluorosilicates were probably not extracted.

7. Analytical Procedures for Particulate from the Andersen Impactor

The fine particulate ash collected by the Andersen Impactor was impinged on stage filters. Gelman nonspectrograde AE glass fiber stage filters having a diameter of 63.5 mm were used for collecting fine particulate. The filters were wrapped in aluminum foil for storage. Figure B-7 represents the analysis procedures used to determine trace elements in the fine particulate. In order to obtain sufficient sample size for analysis, it was necessary to composite samples by tests and plates. Tables B-6 and B-7 give the compositing scheme of the Andersen Impactor samples.

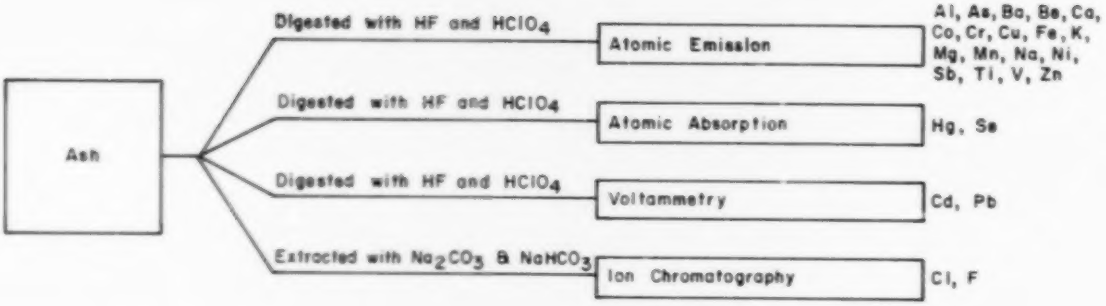

Ash
Digested with HF and HClO4
Atomic Emission
Al, As, Ba, Be, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Sb, Ti, V, Zn
Digested with HF and HClO4
Atomic Absorption
Hg, Se
Digested with HF and HClO4
Voltammetry
Cd, Pb
Extracted with Na2CO3 & NaHCO3
Ion Chromatography
Cl, F

Figure B-7 Analytical procedures for trace element analysis of Andersen Impactor fine particulate

TABLE B-6. COMPOSITING SCHEME FOR ANDERSEN IMPACTOR FINE PARTICULATE FOR DETERMING 22 ELEMENTS

Composite of Field Tests	Composite of Plates	Approximate Particle Size (μm)	Extracted Weight (mg)
1+5	0c+1+2+3	>3	77.90
2+3	0c+1+2+3	>3	95.56
7	0c+1+2+3	>3	36.01
1+5	4+5	1-3	53.27
2+3	4+5	1-3	78.95
7	4+5	1-3	16.30
1+5	6+7+8	0-1	29.63
2+3	6+7+8	0-1	36.90
7	6+7+8	0-1	30.87
Blank	-	-	1.38

TABLE B-7. COMPOSITING SCHEME FOR ANDERSEN IMPACTOR FINE PARTICULATE FOR DETERMINING F AND Cl

Composite of Field Tests	Composite of Plates	Approximate Particle Size (μm)	Field Weight (mg)
6	0c+1+2+3	>3	32.7
6	4+5	1-3	21.16
6	6+7+8	0-1	30.19

7.a Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Na, Ni, Pb, Sb, Se, Ti, V, and Zn in Particulate

The foil containing the filter was dried under an infrared lamp for 10 minutes and desiccated for 30 minutes over silica gel. The tar weight was measured to the nearest one-hundredth of a milligram. The filter was removed from the foil with platinum-tipped forceps and placed in a 100-ml Teflon beaker; any particulate clinging to the foil was removed with absolute ethanol and added to the beaker. Additional ethanol was added to the beaker to cover the filter. The particulate matter was removed from the filter by briefly placing the beaker in an ultrasonic bath. The filter was removed from the beaker with platinum-tipped forceps and returned to the aluminum foil to be dried under an infrared lamp for 10 minutes. After desiccation over silica gel for 30 minutes, the foil and filter were reweighed and the weight extracted was determined by difference.

The next sample to be composited was extracted, dried, and weighed as in the above procedure. This sample was combined with the material in the beaker from the previous sample and the added weight was determined by difference between empty and full sample vessels. The process was repeated for each sample to yield the composited samples listed in Table B-6. After compositing the samples, the ethanol was evaporated to dryness under an infrared lamp and the beaker was stored in a desiccator.[16]

The composited fine particulate (1-100 mg) was digested with 1.5 ml of Ultrex HF and one drop of Ultrex $HClO_4$. The mixture was evaporated slowly, without boiling, to dryness in a sand bath at a temperature not exceeding 220°C. The evaporation was repeated twice with 1.0 ml Ultrex HF and one drop (0.05 ml) Ultrex $HClO_4$. The residue was cooled and moistened with 0.25 ml Ultrex HCl. After a few minutes allowed for dissolution, the mixture was diluted with 2.5 ml of deionized water. The solution was covered with a watch glass and heated just below boiling until all salts and particulate matter had dissolved. When the solution had cooled, the beaker was washed with 1 ml of 5 percent (V/V) Ultrex HCl, and the solution was transferred to a 5.0-ml volumetric flask. The beaker was rinsed with an additional 10 drops (0.5 ml) of 5 percent (V/V) Ultrex HCl and added to the solution in the flask. The solution was diluted to 5.0 ml with 5 percent (V/V) Ultrex HCl, poured into a 10-ml Teflon test tube, and capped with a polyethylene closure.[2]

A 1.5-2.0-ml aliquot of the solution was used to determine the concentration of Ba, Be, Cu, K, V, Ti, Zn, Al, Ca, Cr, Fe, Mg, Mn, Ni, Co, As, and Sb by atomic emission.[1] Another aliquot was used to determine the concentration of Hg[3] and Se[10] by atomic absorption with cold vapor and hydride generating, respectively. A microvapor vessel and microcell were used for generating the atomic mercury, and the microvapor vessel was used to form gaseous selenium hydride.[3] A 1-ml sample was used for Se and a 0.5-ml sample was used for Hg. A 1-ml aliquot of the solution was treated with 2.0 ml of redistilled HNO_3, and the concentrations of Cd and Pb were determined by differential pulse anodic stripping voltammetry beginning with section 8.4 in the footnoted reference.[13]

The extraction and digestion procedures, repeated for an unused non-spectrograde filter, served as a blank in the analysis.

7.b Cl and F in Particulate

Chloride and fluoride were determined on the particulate captured on the filters from test 6. The stage filters were folded and composited according to Table B-7 in a 15-ml graduated centrifuge tube. The composited filters were treated with 4.0 ml of a solution containing 0.0024 M Na_2CO_3 and 0.003 M $NaHCO_3$. The centrifuge tube was sealed with aluminum foil, sonified in a water bath, and heated for an hour to extract the soluble fluoride and chloride. The solution was cooled and about 0.3 ml was withdrawn for the determination of Cl and F by ion chromotography.[14] The results for fluoride are for the free portion only because the fluorosilicates are probably not extracted. Field weights given in Table B-7 were used to determine concentrations of fluoride and chloride in the particulate.

8. Analytical Procedures for ESP Hopper Ash

The anlytical procedures for the determination of trace elements in ESP Hopper Ash are shown in Figure B-8. The ash was removed from sealed containers without further preparation for chemical analysis by the procedures used to determine the 25 elements in the particulate from train 1 inlet to the ESP. (Refer to sections 2.a-g to learn the chemical techniques.)

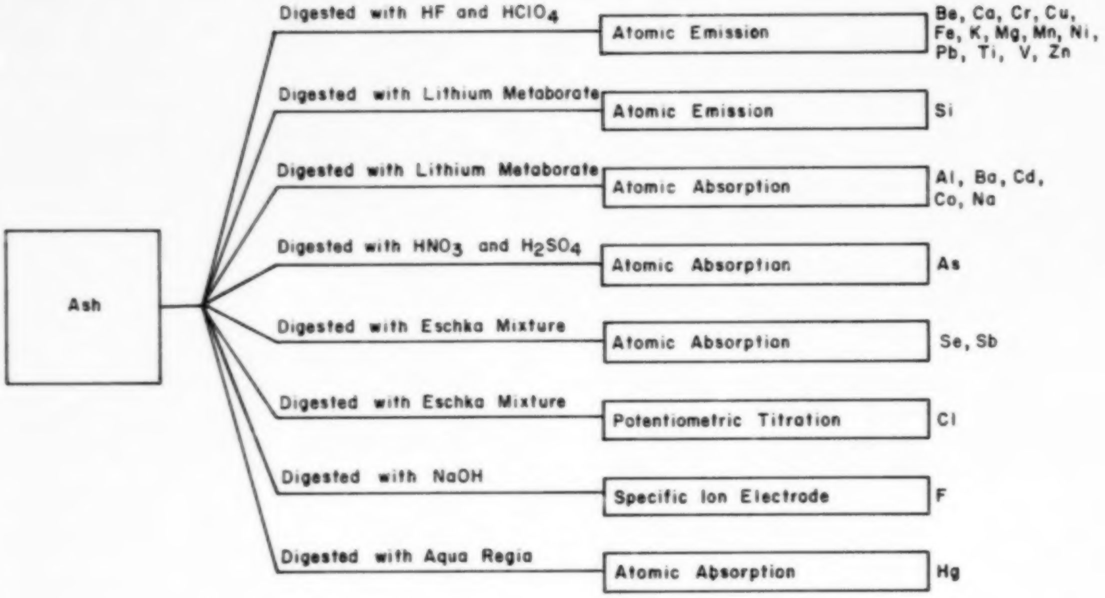

Ash
Digested with HF and $HClO_4$
Atomic Emission
Be, Ca, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, Ti, V, Zn
Digested with Lithium Metaborate
Atomic Emission
Si
Digested with Lithium Metaborate
Atomic Absorption
Al, Ba, Cd, Co, Na
Digested with HNO_3 and H_2SO_4
Atomic Absorption
As
Digested with Eschka Mixture
Atomic Absorption
Se, Sb
Digested with Eschka Mixture
Potentiometric Titration
Cl
Digested with NaOH
Specific Ion Electrode
F
Digested with Aqua Regia
Atomic Absorption
Hg

Figure B-8. Analytical procedures for trace element analysis of ESP hopper ash

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